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SYNTHESIS OF ENERGETIC SINGLE PHASE AND MULTI-PHASE POLYMERS
ANNUAL PROGRESS REPORT FOR 1988

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The synthesis of polyformals from fluoro- and nitrodiols was continued at a low level. New polyformals were prepared from octafluorotriethylene glycol and hexadecafluorodecanediol. Polyformals of a tetranitrodioxatridecanediol with molecular weights $(\bar{M}_N)$ as high as 6000 were prepared.

Additional copolyformals were prepared from fluoro- and nitrodiols with the objective to obtain polymers with the lowest glass transition temperature and highest energy possible for use as soft blocks in TPE (thermoplastic elastomer) synthesis. Copolymers of a hexanitrodioxadiazapentadecanediol and of dinitrodiazaoctanediol with several fluorodiols appear to be the most promising of the new polymers synthesized.

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The synthesis of copolymers of a carboranediol with a fluorodiol and a nitrodiol was studied in some detail and copolymers over a wide monomer ratio were prepared in high yield.

Further efforts were made to prepare acid chloride terminated polyesters from DINOL (tetranitrodioxanonanediol) and malonyl chloride and to characterize the end groups of these polymers. Complete acid chloride termination could not be demonstrated, and attempts to use such polymers for TPE synthesis were terminated.

Several new energetic (nitro) diisocyanates were synthesized for use in TPE synthesis.

A series of 24 segmented polymers were prepared from homopolyformals and copolyformals of fluoro- and nitrodiols ("soft" blocks), prepared this year, by chain extension with diisocyanates. The properties of these polymers vary widely from soft resins to tough elastomers (at room temperature), depending on the choice of soft block and diisocyanate. They exhibit no sharp melting transition but gradually change from an elastomer to a resin on heating.

The previously developed new method for the determination of the absolute number average molecular weight of polymers by GPC, using the differential viscometer detector, was evaluated and found to be useful for homopolymers of a wide molecular weight range.

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1. Please correct the following error in your copy of the subject report: on p. 16, Table 10, the first entry in column 1 should read 9 instead of 13.

Horst Adolph

HORST G. ADOLPH
Synthesis and Formulations Branch

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SYNTHESIS OF ENERGETIC SINGLE PHASE AND MULTI-PHASE POLYMERS

INTRODUCTION

The work described in this report has several objectives. One is to synthesize and characterize energetic single phase polymers (homo- and copolymers), primarily hydroxy-terminated fluoro- and nitro-substituted polyformals and polyesters, which may be useful as binders for cast-curable energetic compositions, and as components for multi-phase segmented (block) copolymers. A second set of objectives is to establish the chemistry for the synthesis of block copolymers from such polydiols and other difunctional polymers, and to provide methods for characterization of the block copolymers produced. The block copolymers to be synthesized are desired to be elastomers in the temperature range of about -10° to +70°C and liquids at temperatures above about 70-90°C. Low melt-viscosities are desired as well. It is believed that these properties will permit and facilitate continuous extrusion processing of propellants which use such polymers as binders. The first objective is supported primarily by the Office of the Chief of Naval Resesarch, while research toward the second objective is supported primarily by the SDI, Office of Innovative Science and Technology. The two efforts are closely related, and funding support overlaps in the area of copolymer synthesis. The results of both programs are therefore presented together.

RESULTS AND DISCUSSION

Homopolyformals.- Additional isolated efforts were conducted in this area to prepare new polyformals of potential interest as soft or hard blocks for block copolymers, or to improve/scale up the preparation of polymers of demonstrated interest for this use.

New fluoropolyformals were prepared from octafluorotriethylene glycol (1) and hexadecafluorodecanediol (2).[1] The polyformals obtained from 1 with CH_2O/H_2SO_4 are low viscosity liquids. Molecular weights determined by GPC are in the range of 3000-6000. Fig. 1 shows a typical GP chromatogram. The

$HOCH_2CF_2OCF_2CF_2OCF_2OH$ (1)

$HOCH_2(CF_2)_8CH_2OH$ (2)

polyformals of 2, obtained similarly with sulfolane as cosolvent, are solids melting near 100°C, potentially useful as hard blocks in block copolymers. The GP chromatograms (Fig. 2) show some irregularities resulting from poor solubility of the monomer and the product in the reaction mixture.

The synthesis of the previously prepared polyformal of diol 3 (3M product #L-9939)[2] was scaled up to the 50g level. This liquid polyformal was expected

$$\left[HOCH_2\overset{CF_3}{\overset{|}{C}}FOCF_2\overset{CF_3}{\overset{|}{C}}FOCF_2CF_2 \right]_2$$

3

to be useful as a soft block; however, the results of GPC and OH analysis indicate that it may not be difunctional: a 50g sample had $\bar{M}_N$ = 2100 by GPC, but OH equivalent weights of 1540 (NMR) and 1350 (isocyanate method); a second, 40g sample had $\bar{M}_N$ = 2570 but an OH equiv. wt. of 3020. This can be explained by the presence of monoalcohols in 3. This would preclude the use of the polyformal of 3 for block copolymer synthesis.

The synthesis of the previously prepared[2] polyformal of diol 4 was also scaled up. It was found (see below) that the 4:1 copolymer of diol 4 with

$$HOCH_2CH_2CH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2CH_2CH_2OH$$

4

octafluorohexanediol had a T_G of -13°C. Since this was only slightly lower than the T_G of the polyformal of 4 itself (-11°C), it was decided to use the latter directly as a soft block for block copolymers. Procedures were found to obtain the polyformal of 4 with several different molecular weight ranges, and the following polymer batches were prepared in yields of about 80%: $\bar{M}_N \approx 3000$, 10g; $\bar{M}_N \approx 4000$, 56g; $\bar{M}_N \approx 7500$, 42g; $\bar{M}_N \approx 9000$, 10g. GP chromatograms are shown in Figs. 3-6. Table 1 illustrates conditions and results of several scale-up runs.

Table 1. Scale-up runs of Polyformals from Diol 4

Monomer (g)	Conditions*	Yield (%)	$\bar{M}_N$ (GPC)	OH Equiv. Wt. (NMR)
6	sulfolane/ dichloromethane (1ml)/ $SnCl_4$ (0.25ml); 104% trioxane	89	3479; 5048 (excl. cyclic formals)	3128
6	same but 90% trioxane only	89	2517; 3375 (excl. cyclic formals)	1750
14.4	same but 96% trioxane; 20°C	90	3350 (excl. cyclic formals)	2230
14.4	sulfolane/dichloromethane (0.75ml)/$SnCl_4$ (0.265ml); 104% trioxane; 20°C	90	5440 (excl. cyclic formals)	3800
5.4	sulfolane/dichloromethane (0.25ml)/$SnCl_4$ (0.265ml); 104% trioxane; 20°C	90	6250 (excl. cyclic formals)	

* amounts are for 1.8g monomer 4

Copolyformals.- It was shown in earlier work[3] that copolyformals could be formed from various combinations of fluorodiols and nitrodiols. ^{1}H-NMR analysis indicated that the copolymers obtained were somewhat segmented: the less acidic diol predominated in the center of the polymer chains, the more acidic (less reactive) diol was concentrated at the ends. This ratio could be changed towards more complete randomization by gradual addition of the more reactive monomer to the mixture of formaldehyde/acid/less reactive monomer. This year's effort was directed mostly toward the synthesis of copolymers useful as energetic soft blocks. It was expected that the combination of a nitrodiol with a fluorodiol would best meet this objective. The formation of copolyformals from the fluorodiols 5 and 6 and the nitrodiols 7 - 10 was therefore pursued further. Copolymers of 5 and 8, and 6 and 8, prepared earlier in ratios from 10/90 to 90/10, were characterized more fully. Data

$HOCH_2(CF_2)_4CH_2OH$ 5

$HOCH_2(CF_2)_3OCF(CF_3)CH_2OH$ 6

$HOCH_2CH_2N(NO_2)CH_2CH_2N(NO_2)CH_2CH_2OH$ 7

$HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$ 8

$HO(CH_2)_3C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2(CH_2)_3OH$ 9

$HOCH_2CH_2N(NO_2)CH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$ 10

obtained are listed in Table 2. Due to signal overlap, it was not possible to

Table 2. Properties of Copolyformals of 5 and 8, and 6 and 8

Feed Ratio	Yield (%)	OH equ. wt.		Overall Monomer Ratio (^{1}H-NMR)	T_G (DSC) [°C]
		GPC estimate	TsNCO method		
5/8					
10/90	>70	1066		9.7/90.3	
20/80	>70	1302		18.2/82.3	14
50/50	85-90	1206	1258	52.2/47.9	
80/20	85-90	1193		79.7/20.3	-22
90/10	85-90	1187	1160		
6/8					
10/90	>70	1174		8.6/91.5	2
50/50	85-90	1237	1335	44.3/55/8	
80/20	75-80	1169		72.3/27/7	-30
90/10	80-85	1171		85.9/14.2	

determine the endgroups by the usual ^{1}H- or ^{19}F-NMR methods. Selected OH equivalent weights were therefore determined by the toluenesulfonyl isocyanate method. Selected GP chromatograms and ^{1}H-NMR spectra of these copolymers are shown in Figures 7-10.

80/20 Copolyformals with $\bar{M}_N$ = 2500 and 2350, respectively, were prepared from diol 9 and the two fluorodiols 5 and 6. The glass transition temperatures of these copolymers were only slightly lower (-13 for 9/5 copolymer) than that of the homopolyformal of 9 (-11°C). Therefore, these copolymers are of little interest as soft blocks.

The copolymerization of diol 10 with 5 and 6 was investigated extensively. $\bar{M}_N$s of 2000 - 3000 were achieved by reaction with trioxane and BF_3 etherate in sulfolane. Results of this work are summarized in Table 3.

Table 3. Copolyformals of hexanitropentadecanediol 10 with fluorodiols 5 and 6

Feed Ratio	Yield [%]	$\bar{M}_N$ (GPC)	T_G (DSC) [%]	Appearance
10/5				
90/10	>85	3940	-	glass
80/20	>85	2900	-	glass
70/30	-	2000; 3500	-	resin
50/50	89	3000	1	resin
10/6				
80/20	>85	3260	-	resin
70/30	>85	2600-2700	10	resin
50/50	-	2800	0	resin

7:3 Copolymers were selected as potential soft blocks in a compromise between low T_G and low fluorine content. The highest MW for the 10/6 copolymer (ratio 7:3) obtained was $\bar{M}_N$ = 2600 - 2700. The preparation of this polymer was scaled up to the 50g level and a total of 60g of $\bar{M}_N$ = 2600 was prepared. Fig. 11 shows the GP chromatogram and Fig. 12 the ^{1}H-HMR spectrum. Figures 13 and 14 show the same data for the 70/30 copolymer of 10 and 5.

Also prepared was a 1:1 copolymer of diols 7 and 6 for comparison of its T_G with that of the corresponding copolymer of 7 and 5. $\bar{M}_N$ by GPC was 1824. The respective glass transition temperatures were -23° and -24°C.

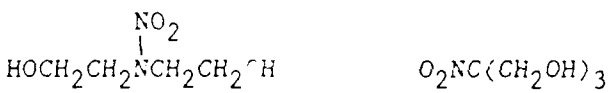
The copolymerization of 5 and 10 with bis(2-hydroxyethyl)-o-carborane, which had been demonstrated previously, was studied in more detail. The copolyformals prepared, and some of their characteristics, are shown in Table 4, selected GP chromatograms and ^{1}H-NMR spectra in Figures 15-16 and 17-18, respectively. The copolymers with 10 are potential high energy components for block copolymers.

Table 4. Copolyformals of bis(hydroxyethyl)-o-carborane and 5 and 10, respectively

Feed Ratio	$\bar{M}_N$ (GPC estimate)	Appearance	Yield (%)
5 Copolymers			
90/10	2074	resin	>75
80/20	1702	resin	>70
65/35	1885	resin	>70
10 Copolymers			
90/10	2290/2950*	hard glass	>80
80/20	2450/3130*	resin	>75
70/30	2150/2890*	resin	>75

* with and without cyclic formals

About 100g of the 97.5/2.5 copolyformal of octafluorohexanediol (5) and 3-nitro-3-azapentanediol (11) were prepared for evaluation as a cast-curable binder in combination with FEFO as plasticizer. The polymer prepared had $\bar{M}_N \approx 2000$. The GP chromatogram is shown in Fig. 19.



11

12

The copolymerization of 6 and 11 was studied briefly. 11 could be incorporated more readily than in the case of 5 and 11, up to 10% or more. However, at the 10% level, $\bar{M}_N$ did not exceed ~1500, and at lower levels (2.5%, 5%), the copolymers were not miscible with FEFO and other energetic plasticizers (the reason for attempting this copolymerization). Similarly, copolymers prepared from the 3M perfluoropolyether diol L-9939 (3) and 7 (ratios 2:1 and 1:1), which had $\bar{M}_N$ 1900-1700, were not miscible with energetic plasticizers. Selected GP chromatograms and ^{1}H-NMR spectra are shown in Figures 19-21.

Attempts were made to copolymerize octafluorohexanediol 5 and nibglycerol 12 in order to obtain a polyformal with functionality >2. However, only homopolymers of 5 were obtained with no incorporation of detectable amount of 12.

Some additional DSC, T_G, and viscosity data obtained for several of the copolymers prepared earlier are listed in Table 5. As expected, T_G and

Table 5. Thermal and Viscosity Properties of Some Copolyformals

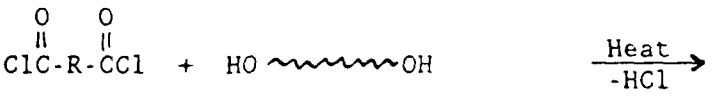
Polymer/$\bar{M}_n$	T_G (°C; DSC)	TMA Onset of Softening (°C)	TGA T10%* (°C)*	Viscosity at 10 Rad/sec (Poise) 50°C	75°C	100°C
FPF-1/2150	-55.7	-40.0	364	61.4	12.6	5.9
5-Co-11 (97.5:2.5)/1954	-58.0	-40.0	334	48.3	11.7	5.2
5-Co-7 (15:85)/1981	-12.3	2.0	276	2825	185.5	37.5
5-Co-7 (30:70)/2096	-14.0	-1.0	277	1686	149.2	27.6
5-Co-7 (50:50)/2075	-23.9	-8.5	276	585.8	74.9	13.5
5-Co-7 (70:30)/2139	-34.7	-18.0	281	257.2	34.3	8.3

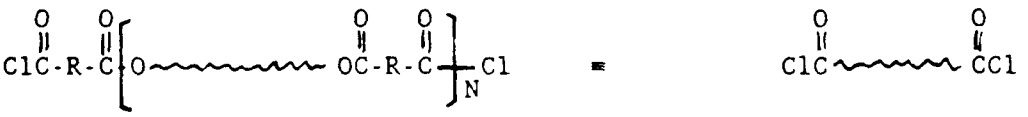
*temperature of 10% weight loss at heating rate of 2°/min.

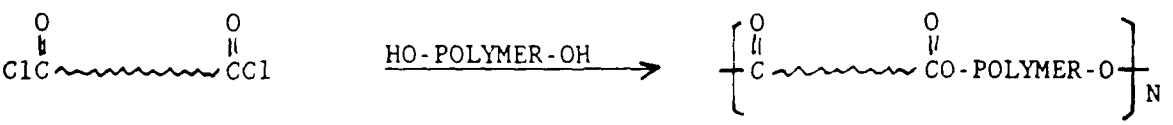
viscosity of the fluorodiol/nitraminediol copolymers increase with increasing nitraminediol content.

Block Copolymer Synthesis.- During the past year, previously initiated approaches to $(AB)_N$ block copolymer synthesis were pursued further. These include (a) the synthesis and reaction of acid chloride-terminated polyesters with a hydroxy-terminated polyester or polyformal; (b) end-capping hydroxy-terminated blocks with a free or semi-blocked diisocyanate, followed by reaction with a second hydroxy-terminated block; (c) reaction of a diisocyanate with hydroxy-terminated blocks. In addition, several new energetic diisocyanates for use in approach (c) were synthesized, and effects of plasticization of $(AB)_N$ block copolymers were studied briefly.

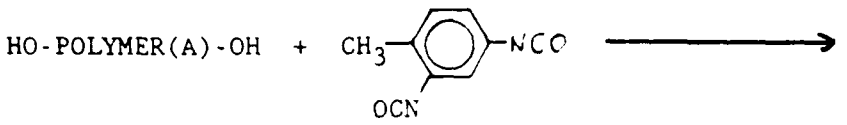
Approach (a):

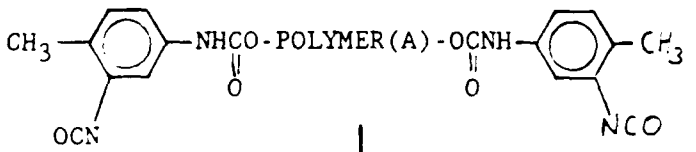


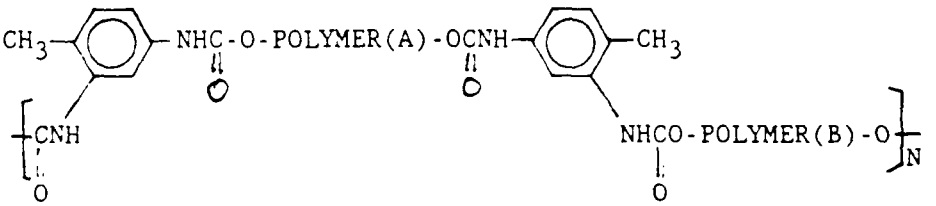




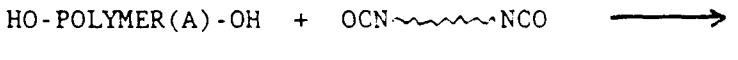
Approach (b):

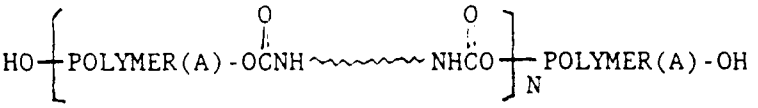






Approach (c):





Approach (a): Previous efforts to prepare block copolymers from acid chloride-terminated nitropolyesters and diols/polydiols were unexpectedly unsuccessful.[2] In an effort to determine the reasons for this result, end group analyses were done for two polyesters. Polymers in the molecular weight range 3000-4000, made by condensation of 13 with excess malonyl chloride, were reacted with trifluoroethanol, t-butanol, and trimethylsilyl azide, respectively. The trifluoroethanol and t-butanol treated polymers were analyzed by ^{1}H-NMR for CF_3CH_2 and $(CH_3)_3C$ content. Molecular weights of 27,000 and 18,000 were obtained (as compared to 3000-4000 by GPC), which indicates that the polymers may not be acid-chloride terminated, or, that the end-capping reaction does not proceed as expected. Similarly, the carbonyl azide-terminated polymer was heated in the presence of 7 and catalyst. There was little increase in molecular weight; an increase would have been expected if the original polymer had been acid chloride-terminated. It appears that this was not the case.

$HOCH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2OH$

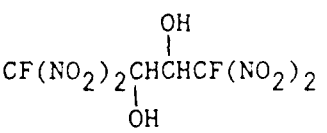
13

Diol 13 was then reacted with 2 equivalents of 4,4-dinitropimeloyl chloride to give low molecular weight oligomers (GPC, Fig. 22) which were clearly, at least in part, acid chloride terminated (^{1}H-NMR, Fig. 23). Subsequent reaction with trifluoroethanol was followed by NMR (disappearance of CH_2COCl) and was found to be very slow (65°C, 17 days, 100% excess CF_3CH_2OH). The resulting product had a molecular weight which was higher than that of the starting material (≈1500 vs. 960) as can be seen by comparing Figs. 22 and 24. The reasons for this increase are not clear. The molecular weight obtained by ^{19}F-NMR end-group analysis was even higher (≈2500), indicating only partial CF_3CH_2 termination.

In view of the above unexplained results, no further work to use the ~~OH + ClC(O)~~ reaction for block-linking is planned.

Approach (b): In our previous work, we demonstrated the formation of $(AB)_N$ block copolymers with TPE properties from TDI-endcapped hexafluoropentanediol polyformal (FPF-1) and nitrodiols/nitropolyformal diols. When 3-nitrazapentane diisocyanate was used in place of TDI, an apparently cross-linked polymer was obtained. This preparation was repeated with distilled diisocyanate and again a cross-linked elastomer resulted.

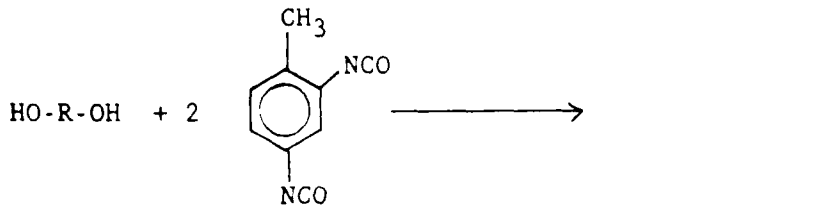
Earlier, TDI-endcapped FPF-1 had been chain-extended with one equivalent of 7 to give an $(AB)_N$ block copolymer.[2] This reaction was repeated with 0.8 equivalents of 7 to test the effect of molecular weight on block-copolymer properties. The molecular weight was lower by GPC (Fig. 25), and the melting point was substantially lower: ~80°C as compared to 95-110° for the 1:1 block copolymer. We also tested the utility of two additional energetic diols, 13 and 14 as "hard blocks".



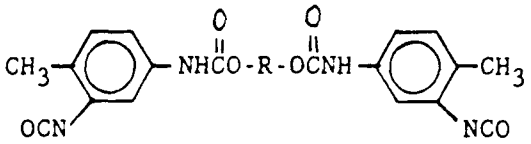
14

No significant chain-extension occurred; degradation (deformylation?) of the diols was the main reaction.

Synthesis of Energetic Diisocyanates: Preliminary work last year showed that chain-extension of hydroxy-terminated soft blocks with TDI gave segmented polymers with "quasi" TPE properties. It was expected that the properties would improve with the use of larger, higher-melting diisocyanates. Last year,[2] 4,4-dinitroheptanedioic azide was synthesized as a precursor for dinitropentane diisocyanate. Using the same approach, 3-nitro-3-azapentanedioic azide was obtained from nitraminodiacetic acid. Additional longer chain diisocyanates 15 and 16 were prepared by end-capping energetic diols 7 and 13 with TDI. Reaction of 15 and 16 with methanol gave the expected urethanes whose ^{1}H-NMR spectra (Fig. 26) were consistent with the assumed structures. GP chromatograms of 15 and 16 show single peaks, indicating that no chain extension occurred during end-capping of the diols with diisocyanate.



7, 13

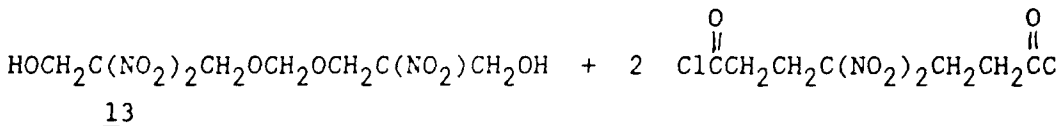


15: R = $CH_2CH_2N(NO_2)CH_2CH_2N(NO_2)CH_2CH_2$

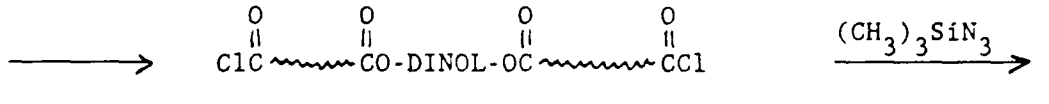
16: R = $CH_2C(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2CH_2$

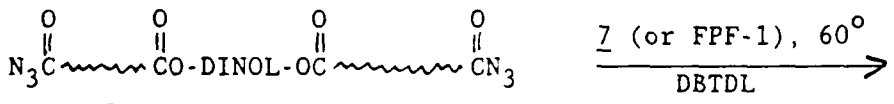
Chain-extension of soft blocks with these isocyanates will provide $(AB)_N$ block copolymers identical in structure with those prepared by approach (b) - end-capping of prepolymer diols with toluene diisocyanate followed by chain-extension with a diol.

An attempt was also made to prepare a diacid diazide, for use in the chain-extension reaction, from the DINOL (13) diester with 4,4-dinitropimeloyl chloride. Reaction of the diisocyanate, generated in situ as above, with 7 and with FPF-1 gave the desired coupling reaction, based on the observed increase of molecular weight in the GP chromatogram. Thus, 17 should be usable for block copolymer synthesis.

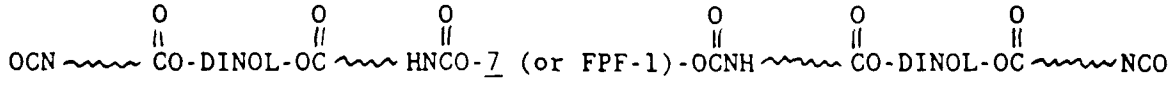


13





17



Approach (c): In the previous work[2] using this approach, FPF-1 had been chain-extended with several diisocyanates, and incipient TPE properties were noted for some of the resulting segmented polymers. This approach was extended to other soft blocks and additional diisocyanates in an effort to prepare phase-separated TPEs with improved properties and to determine variation of properties with structure. A considerable variation of properties with structure of both soft block and diisocyanate, and with the molecular weight of the soft block, was noted. The polymers prepared are listed in Table 6. None of thes materials show narrow melting ranges detectable by DSC. They exhibit elastic properties and visually a temperature range can be identified where this elasticity disappears and the polymers are stirrable; this temperature range is listed in the table as "melting range". Further characterization is in progress. Several samples have been submitted to the University of Massachusetts for characterization of melt behavior and elasticity.

Table 6. Segmented Polymers Prepared by Chain-extension of Hydroxy-terminated Soft Blocks with Diisocyanates

Soft Block ($\bar{M}_N$)	Diisocyanate	Appearance at room temperature	Melting Range [°C]	GPC, Fig. No.
FPF-1 (2100)	3,3-dinitropentane (in situ)	rubbery but soft	70-80°	*
FPF-1 (2100)	3-nitrazapentane	soft, slightly rubbery	75-85°	*
FPF-1 (2100)	toluene-2,4-	resin	-	*
FPF-1 (5400)	3,3-dinitropentane (in situ)	soft, slightly rubbery	<80°	*
FPF-1 (5400)	toluene-2,4-	soft, slightly rubbery	<80°	*
FPF-1 (5400)	3-nitrazapentane	rubbery but soft	>130°	*
FPF-1 (2100)	2-nitrazapropane	soft, barely elastic	75-80°	27
FPF-1 (5400)	2-nitrazapropane	elastic, fairly strong	≈140°	27
5/7 Copolyformal Ratio 70:30	3,3-dinitropentane (in situ)	soft, slightly rubbery	≈70	-
same, Ratio 50:50	same	soft, elastomer	≈70	28
same, Ratio 30:70	same	tough elastomer	≈100	-
same, Ratio 15:85	same	tough elastomer	≈90	-

Table 6. (Con't)

Soft Block ($\bar{M}_N$)	Diisocyanate	Appearance at room temperature	Melting Range [°C]	GPC, Fig. No.
9 Polyformal (3500)	same	elastomer	≈110	29 (typical for most from 9)
same	2-nitro-2-azapropane-1,3-	elastomer	≈130	-
same	toluene-2,4-	elastomer		-
9 Polyformal (6500)	3,3-dinitropentane-1,5-	elastomer	≈130	-
same	2-nitro-2-azapropane-1,3-	elastomer	≈135	-
6 Polyformal (3300)	3,3-dinitropentane-1,5-	resin, barely elastomeric		-
same	2-nitro-2-azapropane-1,3-	resin, barely elastomeric		-
same	toluene-2,4-	soft elastomer		30
Octafluorotriethylene glycol Polyformal (2700)	3,3-dinitropentane-1,5-	resin		-
same	toluene-2,4-	very soft elastomer		31
Poly(2-butoxydioxepane)	3,3-dinitropentane-1,5-	not isolated		32
9 Polyformal (4460)	same	soft elastomer	100-105	-
same (7600)	toluene-2,4-	soft, slightly elastic	100-105	-
same (4460)	15	strong, elastic	115-120	33

Table 6. (Con't)

Soft Block (M_N)	Diisocyanate	Appearance at room temperature	Melting Range [°C]	GPC, Fig. No.
same (7600)	15	elastic		33
same (4460)	16	strong, elastic	-115	-
same (7600)	16	elastic	-110	-

*see reference 2

The elastomers prepared from 9 are the first nitro-substituted TPEs not containing fluorine or other T_G depressants. However, their T_Gs are expected to be between -10 and 0°C and lowering by plasticization or copolymerization may be desirable.

Thermal Characterization: In Table 7 are listed some DSC data for a number of the block copolymers prepared to date. While all polymers show sharp glass transitions for the soft block, only the one which contains a polyformal hard block also shows a second T_G for the hard block. This polymer retains elastomeric properties well beyond the second T_G. None of the DSC curves show sharp melting transitions and only in some cases can broad T_M ranges be identified, as seen in Table 7. This is in agreement with the earlier reported qualitative observations of the melting behavior of these block copolymers which indicate a fairly broad melting range. Selected DSC plots are shown in Figs. 34-36.

Table 7. DSC Data for Various Block Copolymers

Composition Soft Block/Link/Hard Block	T_G (°C)	T_M (°C)
FPF-1 (1900)/TDI/Tetranitrodiazanonanediol (8)	-37.8	-
FPF-1 (5400)/TDI/Tetranitrodiazanonanediol (8)	-44.6	-
FPF-1 (5400)/TDI/Tetranitrodiazanonanediol (8)	-45.6	
Polyformal	28.4	-
FPF-1 (5400)/TDI/Hexanitropentadecanediol (10)	-44.7	-
FPF-1 (5400)/TDI/Dinitrazaoctanediol (7)	-43.8	-
FPF-1 (5400/3-Nitrazapentanediisocyanate/-	-44.0	
FPF-1 (2100)/3,3-Dinitropentanediisocyanate/-	-30.6	70-?
FPF-1 (2150)/2-Nitrazapropanediisocyanate/-	-28.3	
FPF-1 (5400)/2-Nitrazapropanediisocyanate/-	-38.3	

Table 7. (Con't)

Composition Soft Block/Link/Hard Block	T_G (°C)	T_M (°C)
FPF-1 (5400)/TDI/Dinitrazaoctanediol (7); contains less 7	-42.9	60-90
OFHdiol*-DNOdiol** (50:50)/ 3,3-Dinitro-	6.3	50-90?
OFHdiol*-DNOdiol** (30:70)/ pentanedi- /-	7.1	80-90?
OFHdiol*-DNOdiol** (15:85)/ isocyanate	10.1	-

*5

** 7

Plasticization Study: The effect of plasticization of some block-copolymers on their melting points and viscosities was tested qualitatiavely, using the energetic plasticizer FEFO. Presumably, FEFO plasticizes both the hard and soft blocks. Only the block copolymers prepared by end-capping soft blocks with a diisocyanate followed by chain-extension (approach b) were strong enough to retain some elasticity on plasticization with at least 25% FEFO. These results are shown in Table 8. The addition of FEFO had a significant effect on the melting points of these polymers and strongly reduced their elasticity and strength; judging from qualitative observation, the viscosity was not significantly reduced, but quantitative measurements should be obtained.

Table 8. Properties of FEFO-plasticized TPEs

Composition	Melting Range (°C) Without Plasticizer	With Plasticizer
FPF-1 (1900) end-capped with TDI then coupled with 8	90-100	+50% FEFO: resin at r.t.; not elastomeric
same except FPF-1 (5450)	120-125	+10% FEFO: ≃ 115 +50% FEFO: ≃ 80; weak elastomer +100% FEFO: resin
FPF-1 (5450) TDI endcapped, coupled with 8 polyformal	>120	+50% FEFO: 80-90; strong rubber +100% FEFO: resin
FPF-1 (5450) TDI endcapped, coupled with 10	>130	+50% FEFO: 90-100; weak rubber
FPF-1 (5450) TDI endcapped, coupled with 7	95-110	+25% FEFO: 85; weak +50% FEFO: 85; very weak

Polymer Characterization.- Evaluation of the NSWC GPC system for the determination of absolute molecular weight distribution parameters and intrinsic viscosities of unknown polymers has continued. The determination of the absolute number average molecular weight of a polymer sample by this method depends upon the intrinsic viscosity of each eluting species. Consequently, it is essential that the viscometer be able to make accurate intrinsic viscosity determinations over the entire molecular weight region applicable to GPC.

Thus far, comparisons of intrinsic viscosities have been made for narrow distribution polystyrene standards ranging in molecular weight between 1,000 and 1,200,000 of reported data and those obtained using the NSWC viscometer. These measurements were made both on whole polymers, without GPC columns, and again on fractionated polymers, using GPC columns. In both cases, the results were mostly in agreement to within 10% as shown in the following compilation:

		$[\eta]$ (mL/G)	
(i) WITHOUT COLUMNS	MW	OBSERVED	EXPECTED
	45,000	25.50	26.47
	10,000	9.15	9.17
	2,900	5.19	4.94
	890	3.17	2.74
(ii) WITH COLUMNS	1,250,000	296.00	321.00
	760,000	205.00	192.00
	422,000	126.00	133.00
	172,000	69.90	68.50
	108,000	13.20	13.60
	45,400	26.10	26.60
	18,000	13.20	13.60
	6,500	6.58	6.51
	2,900	4.17	4.95
	890	3.17	2.74

In addition, Mark-Houwink constants were measured for polystyrene in THF using the new system and the narrow distribution polystyrene standards of the same molecular weight range. The values again compared favorably with those expected both for the theta (low molecular weight, i.e., <10,000) region and the high molecular weight region (10,000-1,000,000) as shown below:

OBSERVED	EXPECTED
$K\theta$ = 0.076 (mL/G)	0.084 (mL/G)
$\alpha\theta$ = 0.53	0.50
K = 0.0108 (mL/G)	0.0113 (mL/G)
α = 0.728	0.725

As reported previously,[2] a method for the determination of the absolute number average molecular weight of any polymer or copolymer by GPC using only the differential viscometer detector and the universal calibration curve has

been developed. The following equation, whose derivation is not shown here, is the basis for this method:

$$M_N = \frac{3\Phi\ C_I V_I}{4\Pi\ V_s} \sum \frac{Vh_i}{n_{sp_i}}$$

where M_N is the number average molecular weight, Φ is Flory's constant (adjusted to reflect hydrodynamic radius), C_I is the injection concentration, V_I is the injection volume, V_s is the slice volume of the chromatogram, Vh_i is the hydrodynamic volume of each eluting species (obtained from the elution volume and the universal calibration curve), and n_{spi} is the specific viscosity of each eluting species (obtained from the differential viscosity detector output).

Validation of the new method to determine absolute $\bar{M}_N$ and intrinsic viscosity using the differential viscometer as the only detector has continued. Several samples of well characterized commercial polymers with different structures and in the low to medium molecular weight range have been examined with favorable results, Table 9.

Table 9. Comparison of Reported and Measured $\bar{M}_N$ for Various Polymer Samples

Polymer	Sample	$\bar{M}_N$ Reported	$\bar{M}_N$ Measured	$[\eta]$ without GPC Columns	$[\eta]$ with Columns
poly(caprolactone)					
	PCP-310	900	1090	5.49	5.56
	PCP-240	2026	2178	10.09	9.31
	PCP-260	2995	3046	12.06	12.15
poly(propylene glycol)					
	PPG-2000	2000	2040	5.86	5.47
	PPG-4000	4000	4108	10.37	10.42
poly(butadiene)					
	ARCO	2800	2756	15.83	15.82
poly(isoprene)					
	PIP-10200	9681	9330	-	16.26
	PIP-34000	33340	34956	-	36.52
	PIP-135000	129800	125000	-	96.60
polysytrene		119600	114400	-	82.20
poly(methyl methacrylate)		46400	45000	-	31.50

$\bar{M}_N$ of the poly(isoprene) samples were supplied by the vendor. $\bar{M}_N$ of the other samples were determined from their hydroxyl equivalents, most of which were supplied by the vendors. The hydroxy numbers of the PCP-240 and PCP-260 samples were determined at NSWC.

In addition to the commercial samples shown above, a number of polymer samples prepared at NSWC were examined. The results are compared in Table 10 with those obtained using a variety of other methods.

Table 10. Comparison of $\bar{M}_N$ of Various Fluoro- and Nitropolyformals Determined by Different Methods

Polyformal of Diol	^{1}H-NMR	VPO	GPC		
			RI includes cyclic material & monomer	RI excludes cyclic material & monomer	Viscometer
9	2776	1801	1990	2528	2654
10	4164	3008	3538	4046	3973
2	-	1678	2199	3141	2789
5	2248	1889	2096	2096	1901
6	3456	2872	3337	3337	2897
Hexafluoro-pentane	5892	5419	5450	5450	5907

$\bar{M}_N$ is very sensitive to small amounts of low molecular weight impurities. As a result, in those samples where the RI detector showed that low molecular weight impurities were present, the VPO and GPC(RI) values were significantly lower than the values obtained where the low molecular weight impurities were excluded from the GPC(RI) calculations. The NMR results were obtained by measuring the hydroxyl functionality and assuming a molecular functionality of 2. Since the NMR method is not responsive to nonfunctional materials, the NMR results, therefore, correlate well with the GPC(RI) results obtained when the low molecular weight materials were excluded. Because the response of the viscometer increases as a function of the molecular weight, this detector is relatively insensitive to small amounts of low molecular weight material and the $\bar{M}_N$ are similar to those from the RI detector when the low molecular weight materials were excluded from the calculation.

A set of GPC columns suitable for the examination of high molecular weight polymers is presently being calibrated. The examination of a variety of high molecular weight polymers and copolymers, both commercially obtained and made in-house, using the viscometer $\bar{M}_N$ method will be made.

EXPERIMENTAL SECTION

Melting points are uncorrected. Temperatures are in ^{o}C. Microanalyses are by Galbraith Laboratories, Knoxville, Tennessee, NMR spectra were obtained in part on a Varian EM-390 spectrometer, in part on a Varian XL-200 NMR spectrometer. Chemical shifts are in ppm relative to TMS internal standard. Silica gel was Kieselgel 60, 70-230 mesh, throughout.

Gel Permeation Chromatography, General Procedure. Analyses of homopolymers and copolymers were performed using a Waters Model 6000A solvent delivery system, Model U6K injector, Model 440 ultraviolet (UV) absorbance detector, and Model R-401 refractive index detector. A Toyo Soda Micropak H-series guard column, 7.5 cm in length and 0.75 cm in diameter and three Toyo Soda Micropak TSK 3000H size exclusion columns, each 30 cm in length, with inside diameters of 0.75 cm, and packing pore sizes of 1500 A were used. The eluant was deaerated Burdick & Jackson tetrahydrofuran with water content less than 0.01% in order to maximize peak resolution. Solvent flow was nominally 1.0 mL/min. Chart speed was 1.0 cm/min. Data were collected by a DIGITAL MINC microcomputer using a Chromatix CMX-10 dual channel interface module. Data reduction was performed with the Chromatix GPC2 software package. The sample (25-50 mg) was dissolved in 5 mL of deaerated tetrahydrofuran, and approximately 100 μL aliquot was filtered through a Millipore 0.5μ FH type filter and injected into the instrument. Calibration curves were constructed, whenever possible, using the peak positions and molecular weights of the resolved oligomers of each sample.

Some GPC experiments and measurements of intrinsic viscosities using the newly developed methods were carried out using a Waters model 6000A solvent delivery system connected to a Molytek Thermalpulse II flowmeter, and a Waters U6K manual injector. The detector used was a Viscotek model 100 Differential viscometer. The eluant was unstabilized tetrahydrofuran. The flow rate was nominally 1 mL/min. Intrinsic viscosities were determined both with GPC columns connected and without columns connected. GPCs were carried out using Toyo Soda, TSK, H series columns which were 30 cm in length. For polymers whose M_n were below 5000, three columns, each with packing pore size of 1500 A (TSK-3000H) were used. For polymers whose M_n were above 5000, four columns with packing pore sizes of 1500 A (TSK-3000H), 10^4 A (TSK-4000H), 10^5 A (TSK-5000H), and 10^6 A (TSK-6000H) respectively were used.

Data were collected using an IBM PC/AT microcomputer equipped with a Data Translation DT-2805 data acquisition board, and an 80287 math coprocessor chip. The data collection and data reduction software was written in-house using the ASYST version 2.10 scientific programming language. Number average molecular weights were determined using the new algorithm described on p. 15.

Poly(octafluorotriethylene glycol formal).- A solution of 4.466g diol 1 (15.19 mmol) in 2.9 mL of 80% H_2SO_4 and 2.6 mL of dry CH_2Cl_2 (4A sieves) under a N_2 atmosphere was cooled in an ice bath. A solution of .47g of paraformaldehyde (15.6 mmol) in 2 mL of 90% H_2SO_4 was added and the reaction mixture was stirred at room temperature for ~20 hrs. The reaction mixture was poured over 30g of ice and stirred with 30 mL of ether and 1 mL of 30% H_2O_2 for 3 hrs. The ether layer was separated and stirred with 30 mL of 2.5% aqueous KOH and 1 mL of 30% H_2O_2 for ~2 hrs. The ether layer was separated, washed with brine, and evaporated at 45°/20 Torr. Heating to 70°C/0.5 Torr for 3 hrs removed unreacted monomer. The polymer was a pale yellow liquid, obtained in $\geq$80% yield (after monomer removal); ($M_n \approx 3650$).

Poly(hexadecafluorodecanediol formal).- A. H_2SO_4/CH_2Cl_2: Under a N_2 atmosphere, 3.51g of diol 2 (7.60 mmol) was stirred with 2.90 mL of 80% H_2SO_4, 1 mL of 90% H_2SO_4, and 2.6 mL of CH_2Cl_2 (4A sieves) until it formed a homogeneous "slurry". The mixture was cooled in an ice bath and a solution of

.228g of paraformaldehyde (7.60 mmol) in 1 mL of 90% H_2SO_4 was added. The reaction mixture was stirred at room temperature for ~20 hrs. The mixture was poured over 30 g of ice and stirred with 30 mL of ether. The white solid was filtered off, washed with both water and ether, and dried under vacuum over P_2O_5, mp = 100-102°C; $\bar{M}_n \simeq 3600$ (excluding monomer).

B. H_2SO_4/sulfolane: Under a N_2 atmosphere, 3.51g of diol 2 (7.60 mmol) were stirred with 2.5 mL of 80% H_2SO_4 and 2.0 mL of dry sulfolane (4A sieves) until a homogeneous slurry was obtained. The mixture was cooled in an ice bath and a solution of .228g of paraformaldehyde in 1.75ml of 90% H_2SO_4 was added. After stirring overnight at room temperature for ~20 hrs, the reaction mixture was poured over 30g of ice and stirred with 30 mL of CH_2Cl_2 for 1 hr. The white solid was filtered off and washed with H_2O and CH_2Cl_2. The solid was dried under vacuum over P_2O_5; mp = 100-102°C; yield ≃ 91%; $\bar{M}_n \simeq 3150$ (excluding monomer).

Scale Up of Polyformal of Diol 3 (3M L9939).- To a solution of 50.0g of diol 3 (.05 mol) in 19.3 mL of 80% H_2SO_4 and 13.3 mL of 90% H_2SO_4 was added, under a N_2 atmosphere, a solution of 1.26g of trioxane (.042 mol) in 87 mL of dry CH_2Cl_2 (4A sieves), and the mixture was stirred at room temperature for ~20 hrs. The reaction was poured into 300 mL of ice water and was stirred with 300 mL of ether and 12.5 mL of 30% H_2O_2. The ether layer was separated and washed with 300 mL of 2.5% aqueous KOH and 12.5 mL of 30% H_2O_2, and then with 250 mL of water. After stirring with silica gel (15 mL) overnight, the solution was filtered and stripped (50°C/20 Torr); the yield of polymer was ~90%; $\bar{M}_n \simeq 2100$. When 1.35g of trioxane (0.045 mol) was used, a polymer of $\bar{M}_n \simeq 2600$ was obtained.

Scale Up of Poly(4,4,10,10-tetranitro-6,8-dioxatridecane-1,13-diol formal).- To a solution of 14.4g of diol 4 (.0360 mol) and 1.08 of trioxane (.0360 mol) in 12 mL of dry sulfolane (4A sieves) and 8.0 mL of dry CH_2Cl_2 (4A sieves) under a N_2 atmosphere, cooled to 18-20°C, was added 2.0 mL of $SnCl_4$. The mixture was stirred at 20°C for 20-24 hrs, then quenched in 150 mL of H_2O and stirred with 150 mL of CH_2Cl_2 for 1 hr. The organic phase was separated and washed with 100 mL of brine. The CH_2Cl_2 solution was stripped (55°C/20 Torr), the residue was dissolved in 20-25 mL of THF and this solution was added dropwise to 200 mL of vigorously stirred water. The mixture was heated to 60°C and the THF was removed in a stream of N_2. The aqueous phase was decanted and the residue rinsed with fresh water. THe sulfolane-free polymer was dissolved in 150 mL of CH_2Cl_2 and was stirred for 3 hrs with 150 mL of .01 M H_2SO_4 and 7 mL of 30% H_2O_2. The organic phase was separated and stirred with 150 mL of 1% aqueous KOH and 4 mL of 30% H_2O_2 for 3 hrs, separated and washed with brine. After stirring with 10 mL of silica gel overnight, the solution was filtered and stripped at 60°C/~0.5 Torr. The yield of polymer was about 80%; $\bar{M}_n \simeq 3350$ (GPC).

When 1.12g of trioxane, 2.12 mL of $SnCl_4$ and 6 mL of CH_2Cl_2 was used, $\bar{M}_n \simeq 5440$ (GPC) was obtained. With 1.12g of trioane, 2.12 mL of $SnCl_4$, and 2 mL of CH_2Cl_2, M_n was approximately 6250 (GPC).

Poly(4,4,10,10-tetranitro-6,8-dioxatridecane-1,13-diol formal-co-2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol formal), Monomer Ratio 4:1.- A solution of 5.76g of diol 4 (.0144 mol), 1.181g of octafluorohexanediol (5) (4.508×10^{-3} mol) and .482g of trioxane (.0161 mol) in 6.0 mL of dry

sulfolane (4A sieves) and 4.0 mL of dry dichloroethane (4A sieves) under a N_2 atmosphere was cooled in an ice bath and 1.0 mL of $SnCl_4$ was added. The cooling bath was removed and the mixture was stirred at room temperature for about 20 hrs. The reaction was quenched with 60 mL of ice water and was stirred with 60 mL of CH_2Cl_2 for 1 hr. The organic phase was separated, washed with brine, and evaporated at 60°C/20 Torr. The remaining liquid was triturated with 3-4 60 mL portions of water at 55°C (mechanical stirrer) over a 3 day period until no sulfolane could be detected in the ^{1}H-NMR spectrum. The copolymer was redissolved in CH_2Cl_2 and stirred with silica gel (5 mL) overnight. The solution was filtered and stripped at 60°C/20 Torr; the yield was 92%; $\bar{M}_n \approx 2500$ (exluding monomer).

Poly(4,4,10,10-tetranitro-6,8-dioxatridecane-1,13-diol formal-co-2,4,4,5,5,6,6-heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol formal), Monomer Ratio 4:1.- The same procedure was used as given above for the 4/5 copolymer. A copolymer with $\bar{M}_n = 2630$ was obtained.

Poly(3,5,5,11,11,13-Hexanitro-3,13-diaza-7,9-dioxapentadecane-1,15-diol formal-co-2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol formal), Monomer Ratio 9:1.- To a solution of 2.738g diol 10 (5.265×10^{-3} mol), .154g of diol 5 (5.88×10^{-4} mol) and .167g of trioxane in 3 mL of dry sulfolane (4A sieves) was added under a N_2 atmosphere .6 mL of BF_3 etherate. The solution was stirred at room temperature for 20-24 hrs, diluted with 10 mL of CH_2Cl_2, and stirred with 10 mL of water fo 1 hr. Another 10 mL of water was added and the CH_2Cl_2 was evaporated in a stream of N_2 at 35-40°C. The aqueous layer was decanted and the remaining polymer was digested with 20-30 mL portions of water, adding a few mL of CH_2Cl_2 when necessary for stirring. When sulfolane was no longer detected in the ^{1}H-NMR spectrum, the copolymer was dried at 60°C/-0.5 Torr for 5 hrs. The yield was > 85%; $\bar{M}_n \approx 3940$.

The same procedure was used for the preparation of copolymers with monomer mol ratios of 4:1, 7:3, and 1:1 except that 0.8 mL of BF_3 etherate was used in the latter case.

Poly(3,5,5,11,11,13-Hexanitro-3,13-diaza-7,9-dioxapentadecane-1,15-diol formal-co-2,4,4,5,5,6,6-heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol formal).- Diols 10 and 6 were reacted in monomer mol ratios of 4:1, 7:3, and 1:1 using the procedure given above for the 10/5 copolymers. Again, 0.8 mL of BF_3 etherate was used for the 1:1 copolymer.

Scale Up of Poly(10 formal-co-5 formal), Monomer Ratio 7:3.- A solution of 34.25g of 10 (6.586×10^{-2} mol), 7.41g of 5 (2.828×10^{-2} mol) and 2.84g of trioxane in 48 mL of dry sulfolane (4A sieves), prepared under a N_2 atmosphere, was cooled in an ice bath and 9.6 mL of BF_3 etherate was added dropwise. The solution was stirred at 20°C for 20-24 hrs, then quenched in 480 mL of water and stirred with 400 mL of CH_2Cl_2 for 1 hr. The organic phase was washed with 400 mL of brine, then evaporated at 50-60°C/20 Torr. The copolymer/sulfolane mixture was dissolved in 300 mL of MeOAc and stirred with 300 mL of .1 M HCl in brine and 30 mL of 30% H_2O_2 overnight. The organic layer was then stirred with 300 mL of 5% of $NaHCO_3$ and 15 mL of 30% H_2O_2 for 8 hrs. The MeOAc was removed from the organic phase at 60°C/20 Torr and the copolymer was triturated repeatedly with H_2O at 40°C adding CH_2Cl_2 when

necessary for stirring. When sulfolane was no longer detected in the ^{1}H-NMR spectrum, the copolymer was redissolved in MeOAc and dried by stirring with 8 mL of silica gel overnight. The solution was filtered and stripped at 60°C/20 Torr, then 0.5 Torr.

Scale Up of Poly(10 formal-co-6 formal), Monomer Ratio 7:3.- 42.56g of 10 (0.0815 mol), 11.5g of 6 (0.03506 mol), 3.51g of trioxane, 60 mL of sulfolane, and 12.0 mL of BF_3 etherate were reacted as above (10/5 copolymer). The crude polymer was dissolved in 400 mL of MeOAc and treated as above with 400 mL of 0.1 M HCl in brine and 40 mL of 30% H_2O_2, then with 400 mL of 5% aqueous $NaHCO_3$ and 20 mL of 30% H_2O_2. The solution was dried by stirring with 5 mL of silica gel and the polymer was isolated as above.

Poly(3,6-dinitro-3,6-diazaoctane-1,8-diol formal-co-2,4,4,5,5,6,6-heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol formal), Monomer Ratio 1:1.- Under a N_2 atmosphere, 1.25g of 6 (3.81 mmol) and .91g of 7 (3.82 mmol) was dissolved in 2 mL of dry sulfolane (4A sieves) by warming to 60°C. After cooling to room temperature, .23g of trioxane (7.67 mmol) was added. The solution was cooled further with a cold water bath and 1.05 mL of BF_3 etherate was added. After stirring overnight at room temperature, the reaction mixture was diluted with 15 mL of CH_2Cl_2 and stirred with 20 mL of water for 1/2 hr. The organic layer was washed with 15 mL of brine and evaporated (60°C/20 Torr). The remaining liquid was triturated with four 30 mL portions of water over a 36 hr period until no sulfolane could be detected by ^{1}H-NMR. The copolymer was redissolved in CH_2Cl_2, the solution was stirred overnight with .5g of silica gel, filtered and stripped at 60°C/20 Torr for ~3 hrs. The polymer had $M_n \approx 1820$.

Poly[2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol formal-co-bis(hydroxyethyl)o-carborane formal], Monomer Ratio 9:1.- To a solution of 1.388g of diol 5 (5.298×10^{-3} mol) and .140g of the carboranediol (6.03×10^{-4} mol) in 1.5 mL of dry sulfolane, prepared under a N_2 atmosphere with some warming and then cooled to room temperature, was added .201g of trioxane (6.7×10^{-3} mol). The solution was further cooled in an ice bath and .6 mL of BF_3 etherate was added. The solution was stirred at room temperature for 20-24 hrs, diluted with 10 mL of CH_2Cl_2 and mixed with 20 mL of water. The mixture was stirred under a N_2 stream until the CH_2Cl_2 had evaporated. The water was decanted and the remaining copolymer was triturated with water at 40°C until no sulfolane could be detected in the ^{1}H-NMR spectrum. The copolymer was dissolved in CH_2Cl_2, the solution was stirred with ~.5g of silica gel overnight, filtered and stripped at 60°C/20 Torr.

Additional carboranediol copolymers with 5 listed in Table 4 were prepared by the same procedure except that 0.158g (5.27 mmol) of trioxane was used. The same procedure was also used for the preparation of the carboranediol copolymers with diol 10 listed in Table 4; 0.158g (5.27 mmol) of trioxane and 3 mL of sulfolane was used for these reactions.

Scale Up of Poly(2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol formal-co-3-nitro-3-azapentane-1,5-diol formal), Monomer Ratio 97.5:2.5.- A solution of 58.500g of diol 5 (.2233 mol), .858g of nitrazapentanediol (5.27×10^{-3} mol) and 6.870g of trioxane (.229 mol) in 60.0 mL of dry sulfolane (4A sieves) under a N_2 atmosphere was cooled in an ice bath and 54.0 mL of BF_3 etherate was added. The mixture was stirred overnight at room temperature, diluted

with 300 mL of CH_2Cl_2, and stirred with 400 mL of water for 1 hr. The organic layer was separated and washed with 350 mL of brine, the solvent was evaporated at 60°C/20 Torr, and the remaining polymer was triturated with 150 mL portions of water at 55°C until no sulfolane could be detected in the ^{1}H-NMR spectrum. The copolymer was dissolved in 300 mL of CH_2Cl_2, stirred with 300 mL of .07 N H_2SO_4 and 60 mL 30% H_2O_2 for 3 hrs, and then stirred with 300 mL of 1% aqueous KOH and 30 mL of 30% H_2O_2 for 3 hrs. The polymer solution was stirred with 15 mL of silica gel overnight, filtered and stripped at 60°C/20 Torr. The yield was > 90%; $M_n \approx 2000$.

Poly(2,4,4,5,5,6,6-heptafluoro-2-trifluoromethyl-3-oxaheptane-1,7-diol formal-co-3-nitro-3-azapentane-1,5-diol formal), Monomer Ratio 97.5:2.5.- To a solution of 2.445g of diol 6 (7.454×10^{-3} mol), 0.31g of nitrazapentane-diol (2.07×10^{-4} mol) and .231g of trioxane (7.70×10^{-3} mol) in 2.0 mL of dry sulfolane (4A sieves) under a N_2 atmosphere was added 1.8 mL of BF_3 etherate, and the mixture was stirred overnight at room temperature. The reaction mixture was diluted with 15 mL of CH_2Cl_2 and stirred 1 hr with 20 mL of H_2O. After separation and washing with 15 mL of brine, the CH_2Cl_2 was evaporated at 60°C/20 Torr and the remaining liquid was triturated with H_2O until no sulfolane could be detected by ^{1}H-NMR. The copolymer was dissolved in CH_2Cl_2 and stirred with ~6 mL of silica gel overnight. The solution was filtered and stripped at 60°C/20 Torr. The yield of copolymer was ~91%; $M_n \approx 1980$.

The same procedure was used to prepare copolymers of 6 with nitrazapentanediol in monomer ratios of 95:5 and 90:10, respectively.

Nitrimino-bis(acetyl azide).- A mixture of 5.34g of nitrimino-bis(acetic acid) (30 mol), 8.75 mL (~120 mol) of $SOCl_2$, .46 mL of DMF, and 60 mL of dichloroethane was heated to 60°C and stirred for 2 hr. The mixture was cooled in an ice bath and washed twice with 20 mL of ice cold water, then with 20 mL of ice cold brine. The solution was dried ($MgSO_4$) and evaporated (40°C/20 Torr) to a yellow oil which crystallized when scratched. The solid was triturated with 15 mL of CCl_4 and filtered to give 3.6g (56%) of a pale yellow solid. 1.5g of the crude acid chloride was recrystallized from 150 mL of CCl_4 under exclusion of moisture. After drying under vacuum, the acid chloride was dissolved in 11 mL of MeCN. Trimethylsilyl azide, 2.2 mL, was added to the cooled solution and the mixture was stirred at room temperature for 2 hrs. The solvent was removed at room temperature/20 Torr, the yellow oil was dissolved in 4 mL of CCl_4, diluted with 4 mL of isopropyl ether, and held at -15°C overnight. The solid was filtered off, recrystallized from ether/isopropyl ether, and dried in vacuo over P_2O_5; mp 69°C; yield 0.84g (53%, from acid chloride).

End-capping of 3,6-dinitro-3,6-diazaoctane-1,8-diol (7) with Toluene-2,4-diisocyanate.- To a solution of 2.00g of anhydrous diol 7 (8.40×10^{-3} mol) in 15 mL of dry acetone (4A sieves) under a dry N_2 atmosphere was added 7.2 mL of toluene-2,4-diisocyanate and ~1 μL of dibutyltin dilaurate. The mixture was stirred at 30°C for 65 hrs, cooled to room temperature, and diluted with 10-15 mL of dry hexanes (4A sieves). The white solid was filtered off under N_2 and washed several times with dry hexanes. It was dried under vacuum and stored over P_2O_5; mp 159-161°C.

End-capping of DINOL (13) with Toluene-2,4-diisocyanate.- To a solution of 2.0g of anhydrous DINOL in 10 mL of dry acetone was added 5.0 mL of toluene-2,4-diisocyanate and 1 μL of dibutyltin dilaurate and the mixture was stirred at 30°C for 65 hrs. After cooling to room temperature, 30 mL of dry hexanes (4A sieves) was added with vigorous stirring. The yellow oil was allowed to settle and the solvents were decanted. The resin was washed with 5-6 15 mL portions of dry hexanes under a N_2 atmosphere. Residual solvent was removed under vacuum to leave a viscous resin which was stored under N_2.

In Situ Preparation (and Reactions) of a Diisocyanate from 4,4-Dinitropimeloyl Chloride/DINOL (13) 2:1 Diester.- Under a N_2 atmosphere 5.74g (0.02 mol) of 4,4-dinitropimeloyl dichloride in 15 mL of dry dichloroethane was heated at 55°C, and 3.44g (0.01 mol) of DINOL (13) was added. Heating was continued at 55-60°C for 4 days, then at 70°C overnight. The solvent was removed in vacuo ($\leq$ 0.5 Torr) at 50°C.

A 1.253g aliquot of the above material was redissolved in 5 mL of dry dichloroethane with heating. The solution was cooled in an ice bath and 0.44 mL (0.38g) of trimethylsilyl azide was added. The mixture was stirred at room temperature for 24 hrs when the solvent was blown off with a stream of nitrogen. The residue was triturated with 10 mL of hexane which was decanted. 5 mL of dichloroethane, 0.35g of 7 and 1 μL of dibutyltin dilaurate was added to the residue and the mixture was heated to 60°C for 3 days.

In a similar experiment, 1.15g of dinitropimeloyl dichloride was reacted with 0.69g of 13 by heating in 5 mL of dichloroethane at 55-60° for 13 days. The crude diester was then reacted with 0.40 mL of trimethylsilyl azide at room temperature overnight. After removal of solvent and rinsing as above, a solution of 7.71g of hexafluoropentanediol polyformal ($\bar{M}_n \simeq 5450$) in 10 mL of warm dichloroethane and 1 μL of dibutyltin dilaurate was added and the mixture was heated at 60°C for 5 days.

Chain Extension of Difunctional Hydroxy Terminated Polyformals with 3,3-Dinitropentane-1,5-diisocyanate (DNPDI); General Procedure.- In a 15 mL 3-neck flask under a N_2 atmosphere was placed 2.108g (6.023×10^{-4} mol) of a polyformal of 9 ($\bar{M}_n \simeq 3500$), 3.7 mL of dry dichloroethane, 0.181g (6.03×10^{-4} mol) of 4,4-dinitroheptanedioic azide, and 0.5 μL of dibutyltin dilaurate. The mixture was stirred to dissolution, then heated and stirred at 68°C for 4 days. The temperature was decreased to -40°C, 1 mL of MeOH was added, and stirring was continued overnight. The solvents were removed in vacuo (0.5 Torr) at 60°C.

The following polymers listed in Table 6 were prepared by the same procedure:

9 polyformal ($\bar{M}_n \simeq 6250$)/DNPDI
6 polyformal ($\bar{M}_n \simeq 3330$)/DNPDI
1 polyformal ($\bar{M}_n \simeq 2720$)/DNPDI

Poly(2-butoxydioxepane)($\bar{M}_n \simeq 3000$); 1.253g of polymer was used, the solvent was toluene (3 mL), 1 μL of dibutyltin dilaurate was used, and the reaction temperature was 90°C

For the following polymers of Table 6, the procedure was the same but the reaction temperature was 50°C:

9 polyformal ($\bar{M}_n \simeq 4460$)/DNPDI
Poly(5 formal-co-7 formal) (Ratio 7:3, $\bar{M}_n \simeq 2150$)/DNPDI
(Ratio 1:1, $\bar{M}_n \simeq 2100$)/DNPDI
(Ratio 3:7, $\bar{M}_n \simeq 2050$)/DNPDI
(Ratio 15:85, $\bar{M}_n \simeq 2000$)/DNPDI

Chain Extension with 2-Nitro-2-azapropane-1,3-diisocyanate (NP-DI), General Procedure.- In a 15 mL 3-neck flask under a N_2 atmosphere was placed 1.768g (5.051×10^{-4} mol) of a polyformal of 9 ($\bar{M}_n \simeq 3500$), 3.7 mL of dichloroethane, 0.115g (5.04×10^{-4} mol) nitrimino-bis(acetyl azide), and 0.4 μL of dibutyltin dilaurate. The mixture was stirred and heated to 58°C for 4 days. The temperature was decreased to 45°C, 1 mL of MeOH was added, stirring was continued overnight, and the solvents were removed in vacuo (0.5 Torr) at 60-65°C for several hrs.

Similarly prepared were the following polymers of Table 6:

9 polyformal ($\bar{M}_n \simeq 6250$)/NPrDI
6 polyformal ($\bar{M}_n \simeq 3330$)/NPrDI

Chain Extension with Toluene-2,4-Diisocyanate (TDI), General Procedure.- In a 15 mL 3-neck flask under a N_2 atmosphere was placed 1.214g (3.469×10^{-4} mol) of a polyformal of 9 ($\bar{M}_n \simeq 3500$), 3.5 mL of dry dichloroethane, 0.049 mL of TDI (3.47×10^{-4} mol) and 0.4 μL of dibutyltin dilaurate. The mixture was stirred 24 hrs at room temperature, 1 mL of MeOH was added, and stirring was continued overnight. The solvents were removed at 60°C/0.5 Torr.

This procedure was also used for the following polymers listed in Table 6:

1 polyformal ($\bar{M}_n \simeq 2720$)/TDI
6 polyformal ($\bar{M}_n \simeq 3330$)/TDI; used 2.375g polymer, 4 mL of dichloroethane and 2 mL of Freon 113 as solvent, and heated to 65°C for 5-6 days
9 polyformal ($\bar{M}_n \simeq 7600$)/TDI; reaction temperature was 30°C

Chain Extension with 15.- To a solution of 2.322g (5.21×10^{-4} mol) of a polyformal of 9 ($\bar{M}_n \simeq 4460$) and 0.305g (5.20×10^{-4} mol) of 15 in 5 mL of dry sulfolane (4A sieves) was added 1 μL of dibutyltin dilaurate and the mixture was stirred 48 hrs at 30°C. 1 mL of MeOH was added, stirring was continued overnight, the mixture was diluted with 20 mL of THF and added dropwise to 175 mL of vigorously stirred water. The THF was evaporated in an air stream and the water was decanted. The remaining polymer was dissolved in CH_2Cl_2, stirred with 0.5g silical gel overnight, and the solution filtered and stripped (60°C/20 Torr, then 0.5 Torr).

The same procedure was used with a polyformal of 9 having $\bar{M}_n \simeq 7600$.

Chain Extension with 16.- Under a N_2 atmosphere 2.294g (5.14×10^{-4} mol) of a polyformal of 9 ($\bar{M}_n \simeq 4460$) and 0.368g (5.32×10^{-4} mol) of 16 was dissolved in 7 mL of dry dichloroethane, 1 μL of dibutyltin dilaurate was added, and the solution was stirred for 48 hrs at 30°C. One mL of MeOH was

added and stirring was continued overnight. The solvents were removed at 60°C/20 Torr.

The same procedure was used with a polyformal of 9 with $\bar{M}_n \simeq 7600$.

References

1. Synthesized by Exfluor Corp., Austin, TX, under an SSPO-sponsored SBIR program.

2. H. G. Adolph, J. M. Goldwasser, D. A. Cichra, L. A. Nock, and M. Chaykovsky, "Synthesis of Single Phase and Multi-Phase Polymers", Annual Progress Report for 1987 to SDIO/IST and OCNR, Naval Surface Warfare Center, March 1988.

3. H. G. Adolph, J. M. Goldwasser, and D. A. Cichra, "Synthesis of Energetic Single Phase and Multi-Phase Polymers", Annual Progress Report for 1986 for the Office of Naval Research and SDIO/IST, Naval Surface Warfare Center, March 1987.

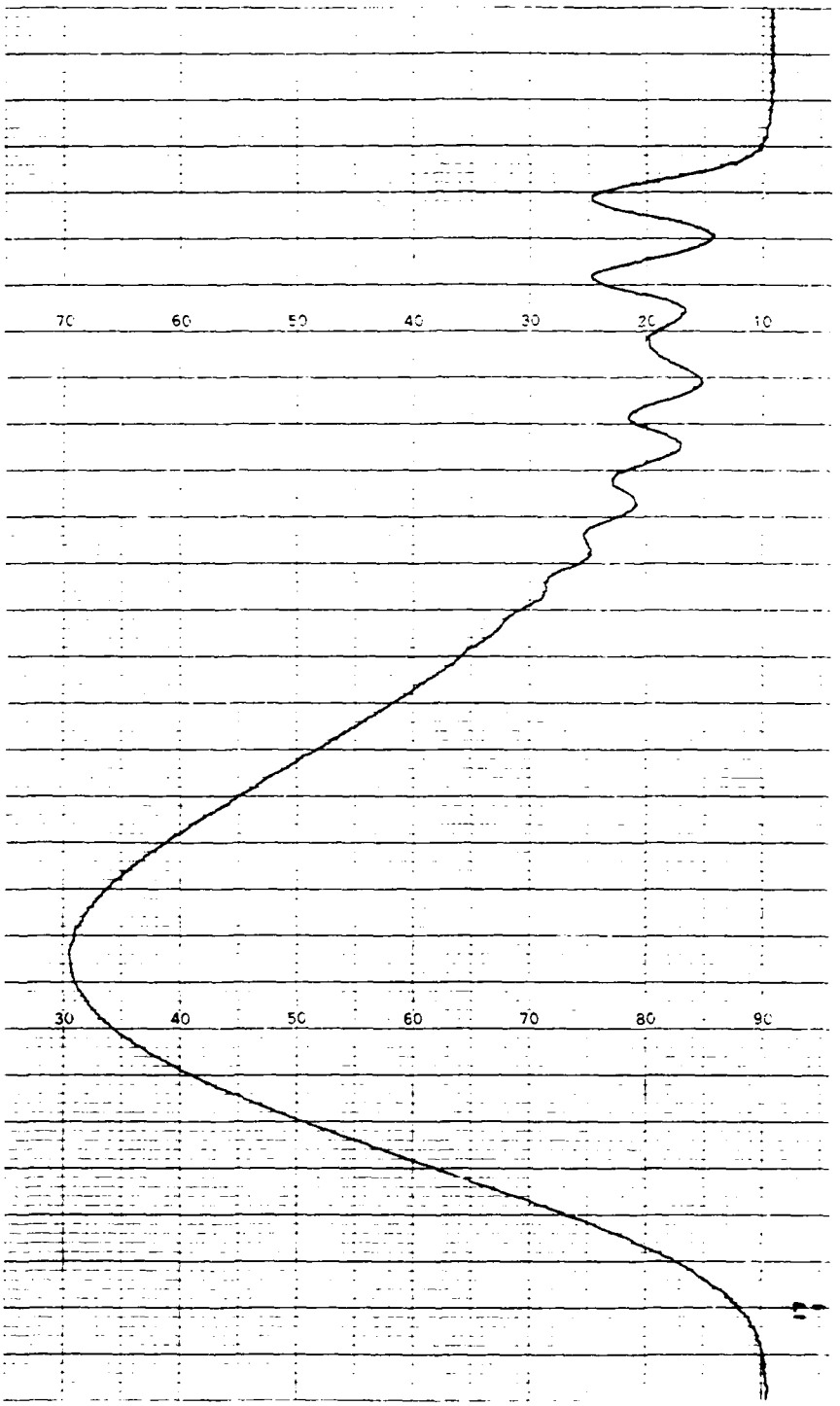


Fig. 1. GP Chromatogram of a Polyformal of Octafluorotriethyleneglycol (1)

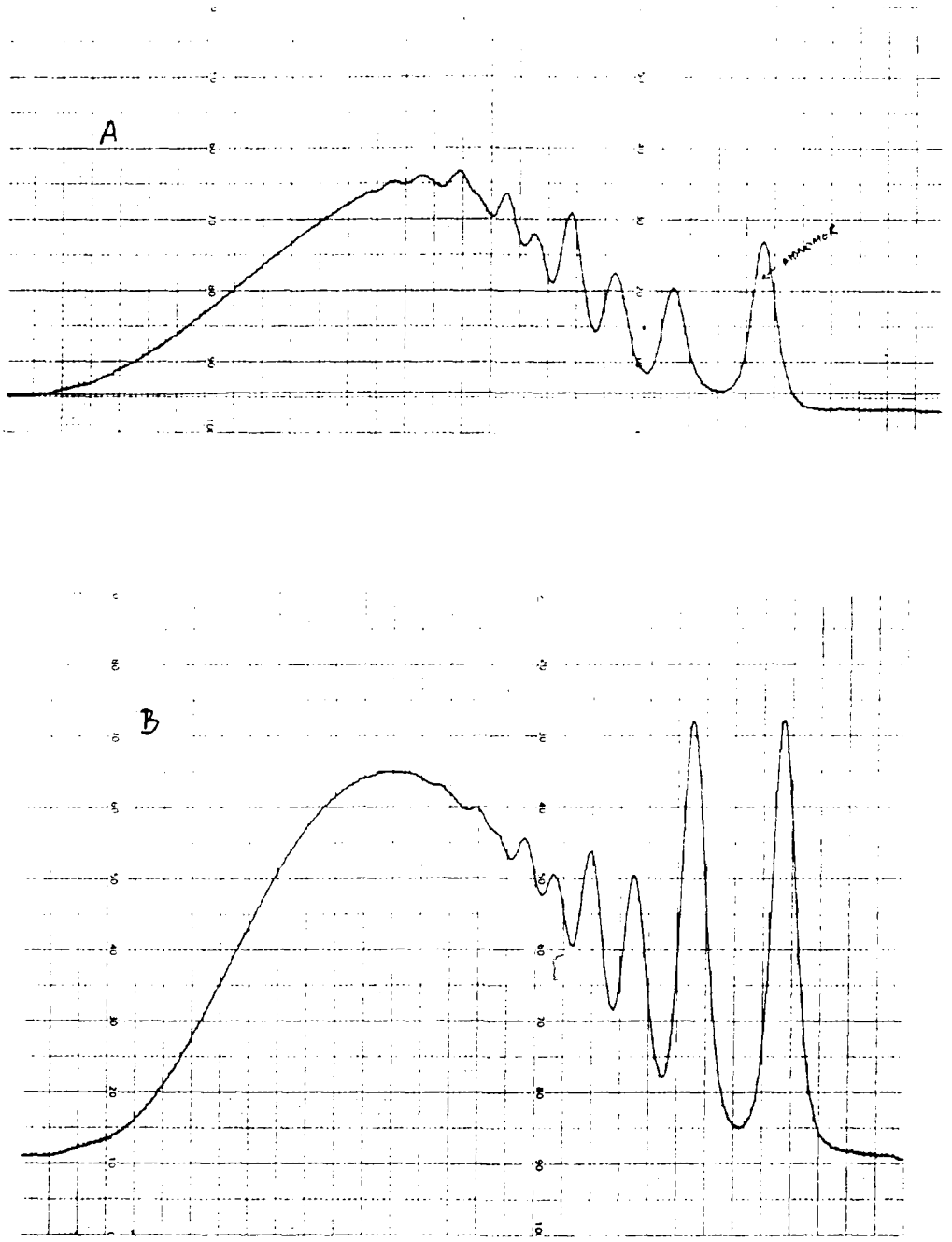


Fig. 2. GP Chromatograms of Polyformals of Hexadecafluorodecanediol (2); (A) from H_2SO_4/CH_2Cl_2, (B) from H_2SO_4/Sulfolane

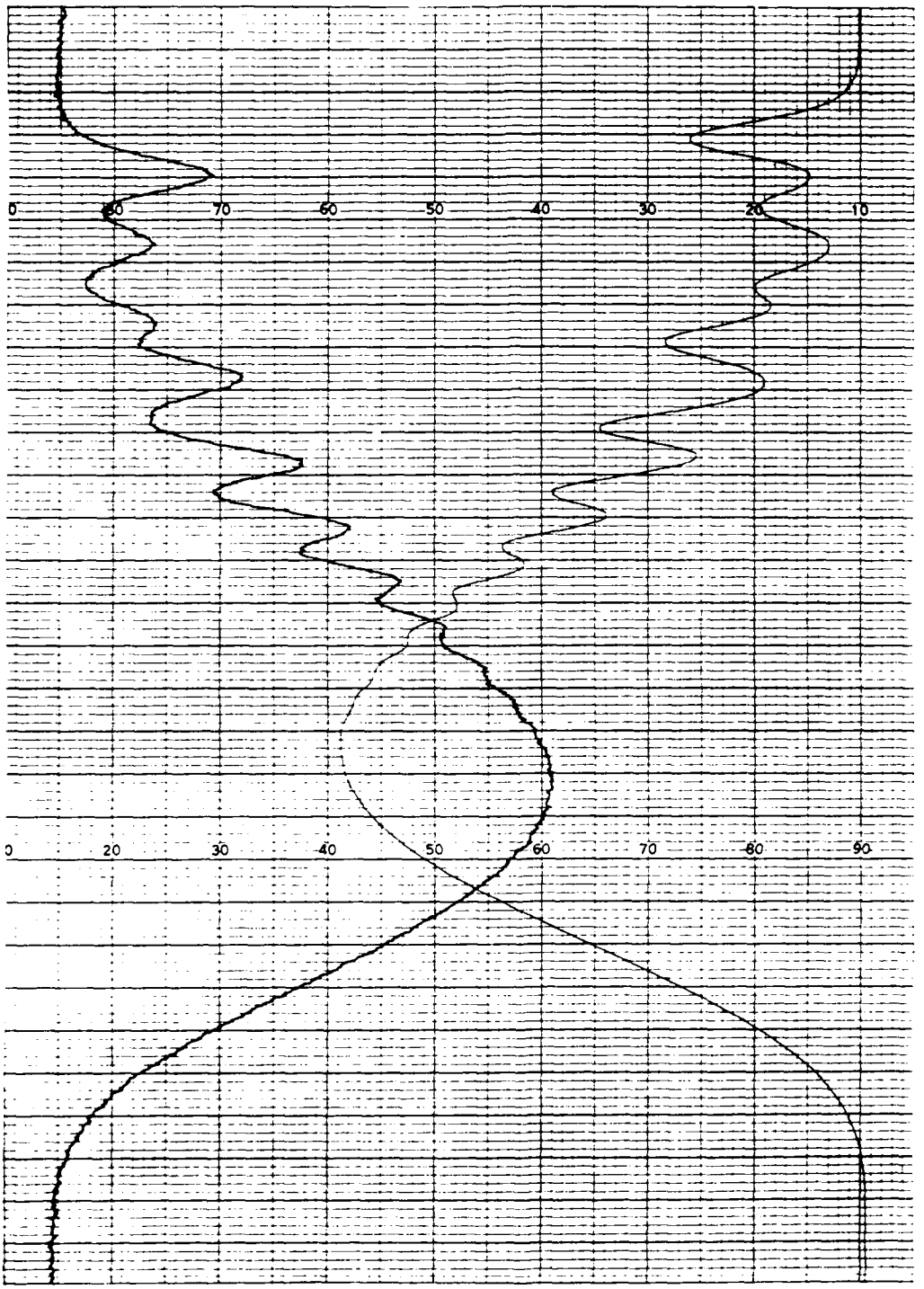


Fig. 3. GP Chromatogram of a Polyformal of Tetranitrotridecanediol 4 ($\bar{M}_N \approx 3000$)

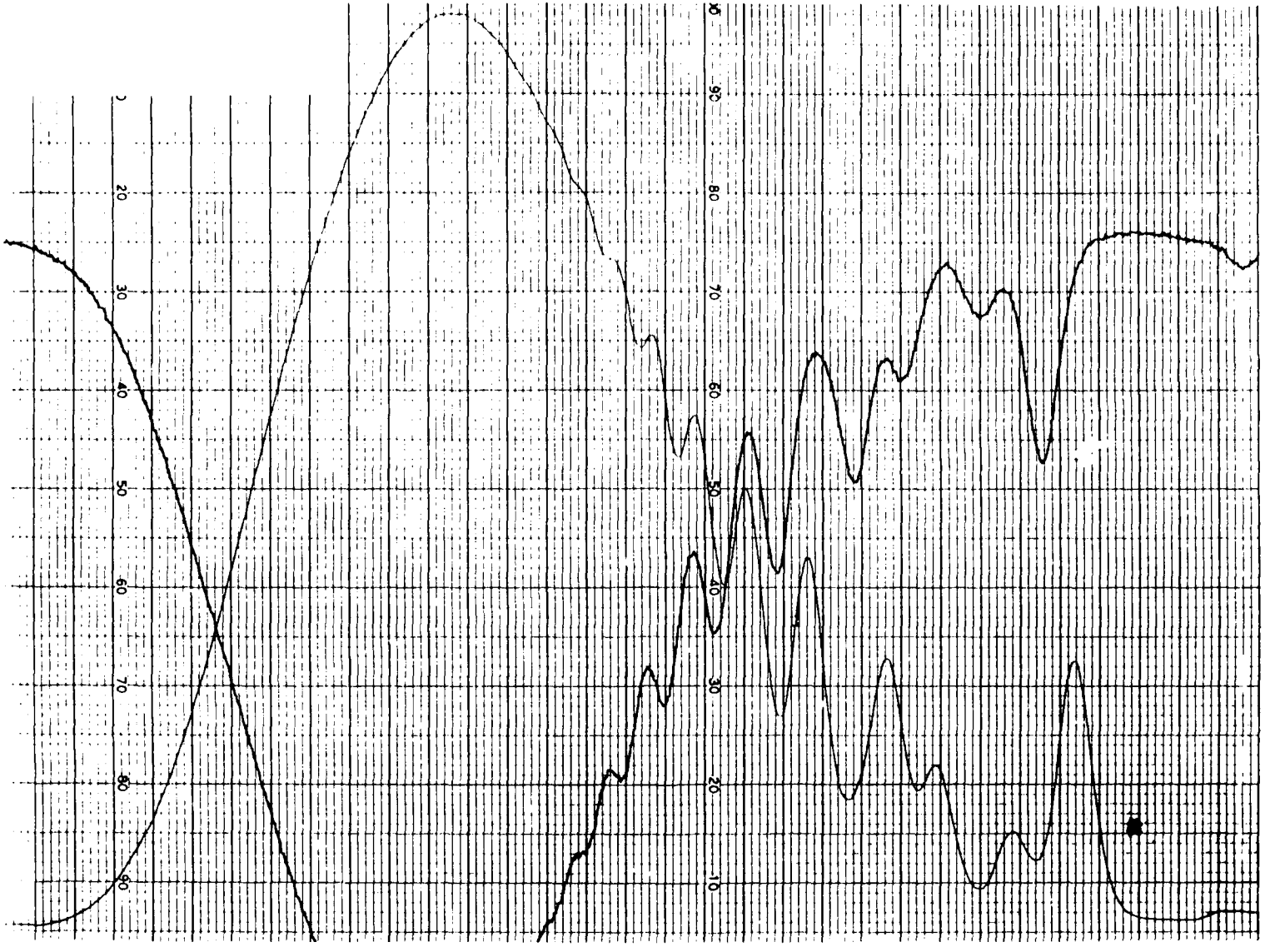


Fig. 4. GP Chromatogram of a Polyformal of Tetranitrotridecanediol 4 ($\bar{M}_N \simeq 4000$)

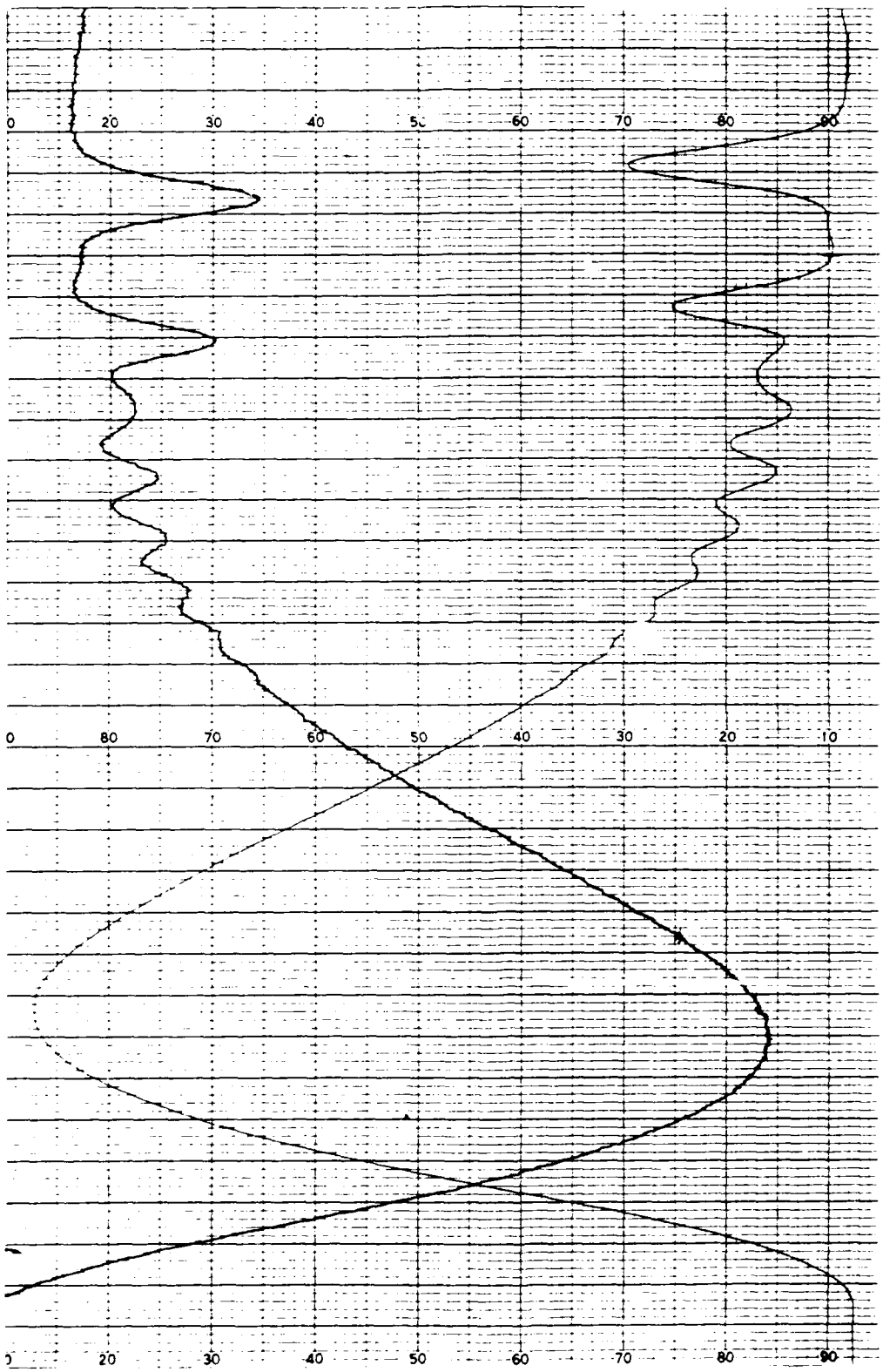


Fig. 5. GP Chromatogram of a Polyformal of Tetranitrotridecanediol 4 ($\bar{M}_N \simeq 7500$)

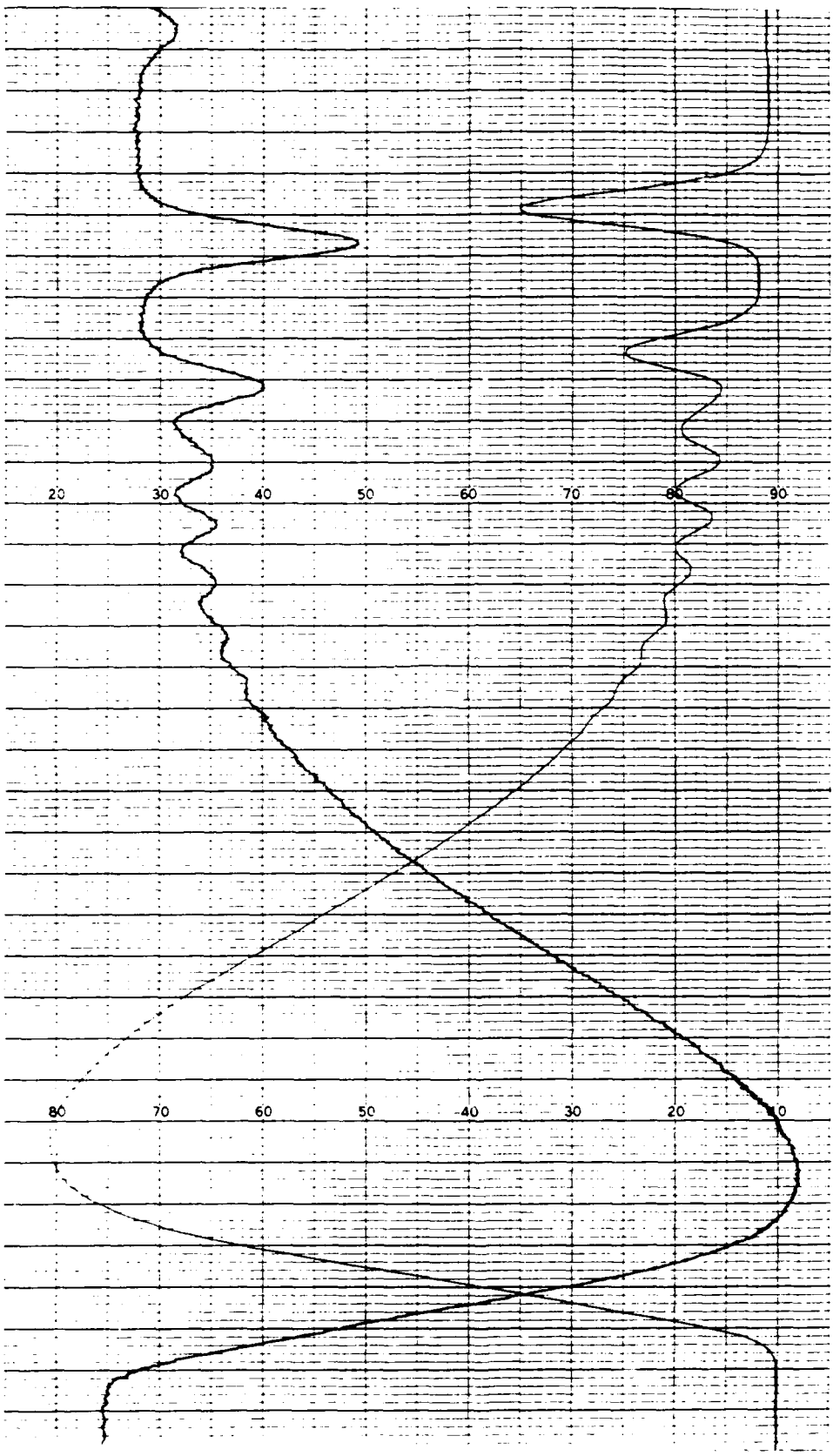


Fig. 6. GP Chromatogram of a Polyformal of Tetranitrotridecanediol 4 ($\bar{M}_N \simeq 9000$)

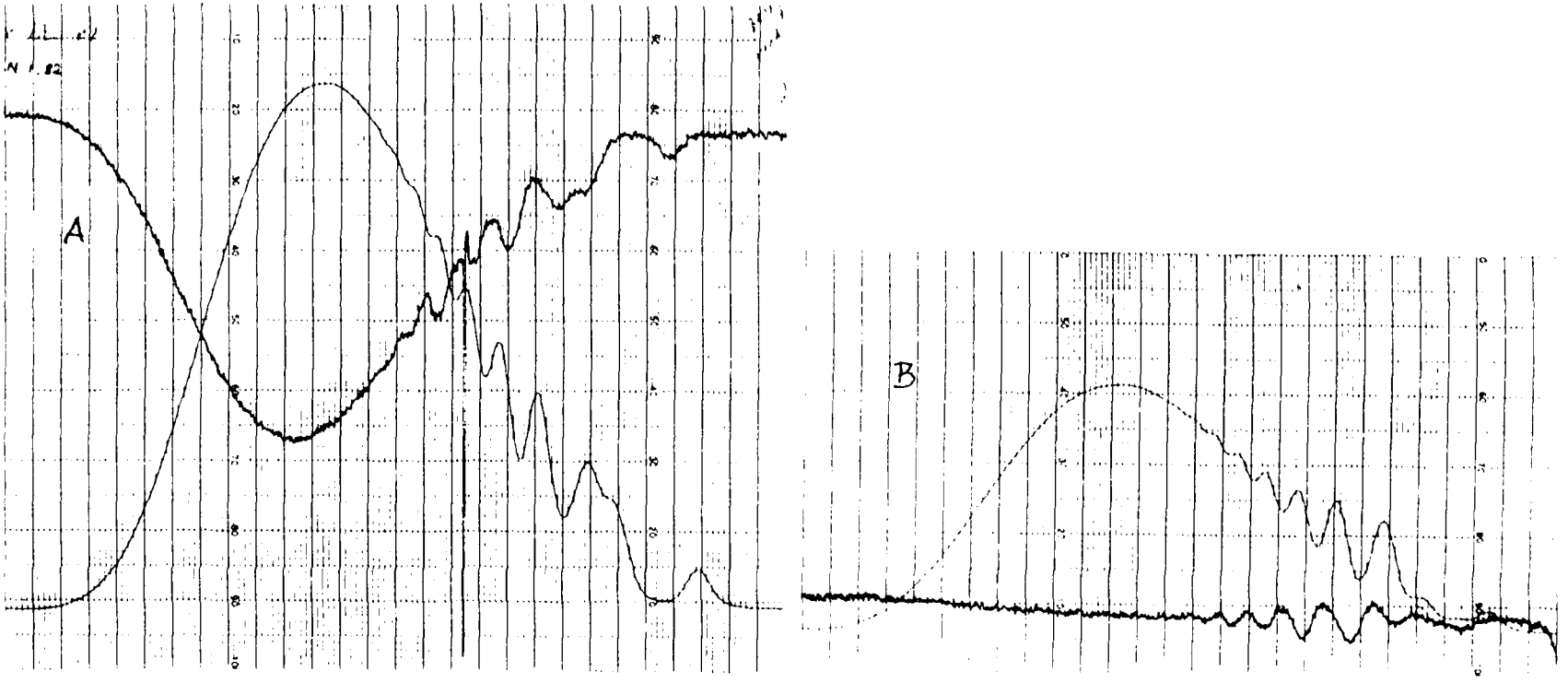


Fig. 7. GP Chromatograms of Copolyformals of Octafluorohexanediol 5 and Tetranitrononanediol 8; A: 20/80; B: 80/20

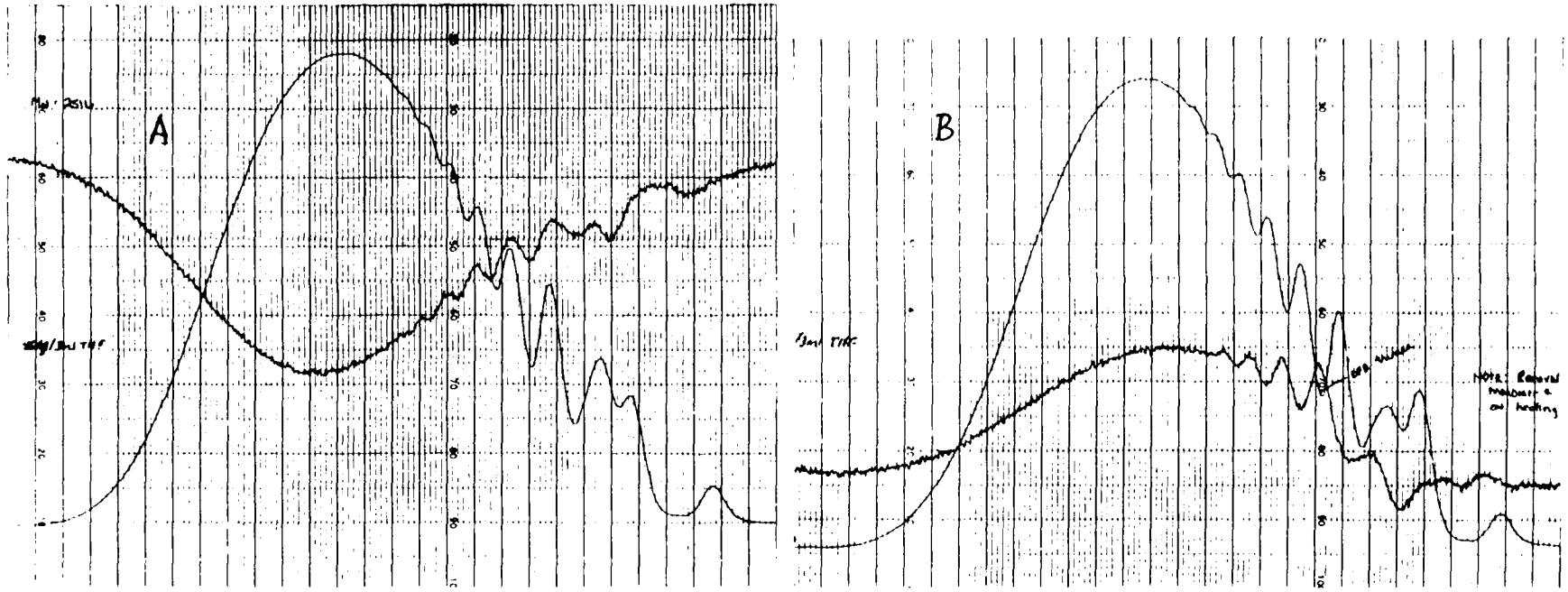


Fig. 8. GP Chromatograms of Copolyformals of Decafluoroheptanediol 6 and Tetranitrononanediol 8; A: 50/50; B: 80/20

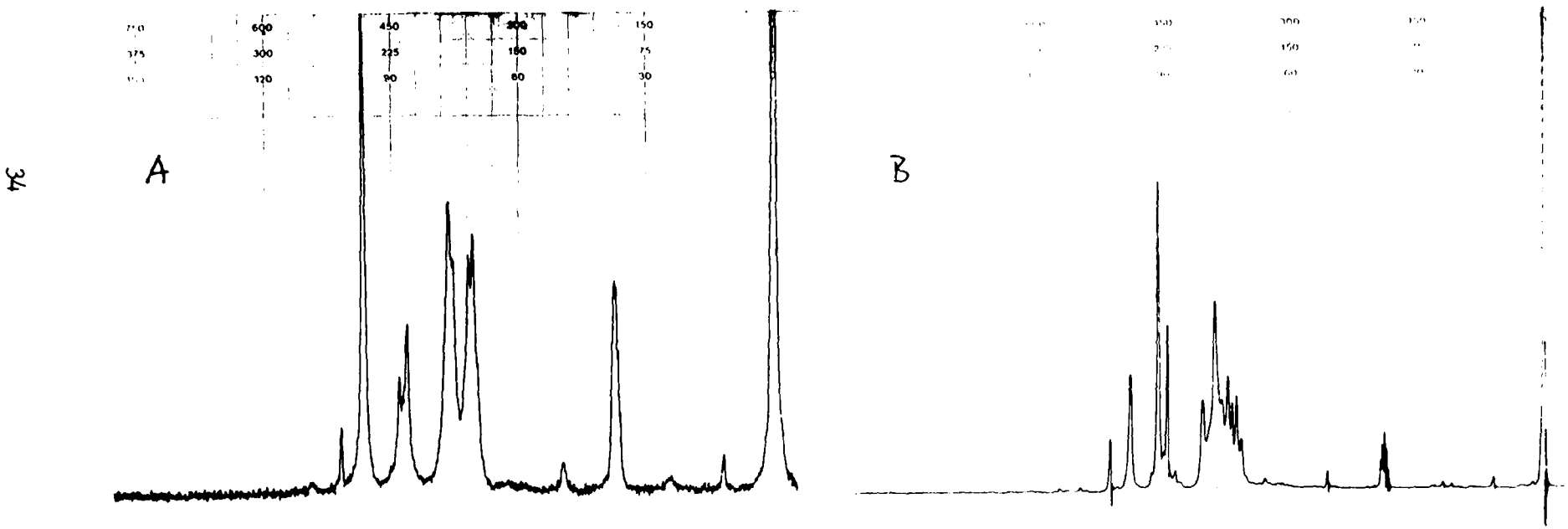


Fig. 9. ^{1}H-NMR Spectra of Copolyformals of Octafluorohexanediol 5 and Tetranitrononanediol 8; A: 20/80; B: 80/20

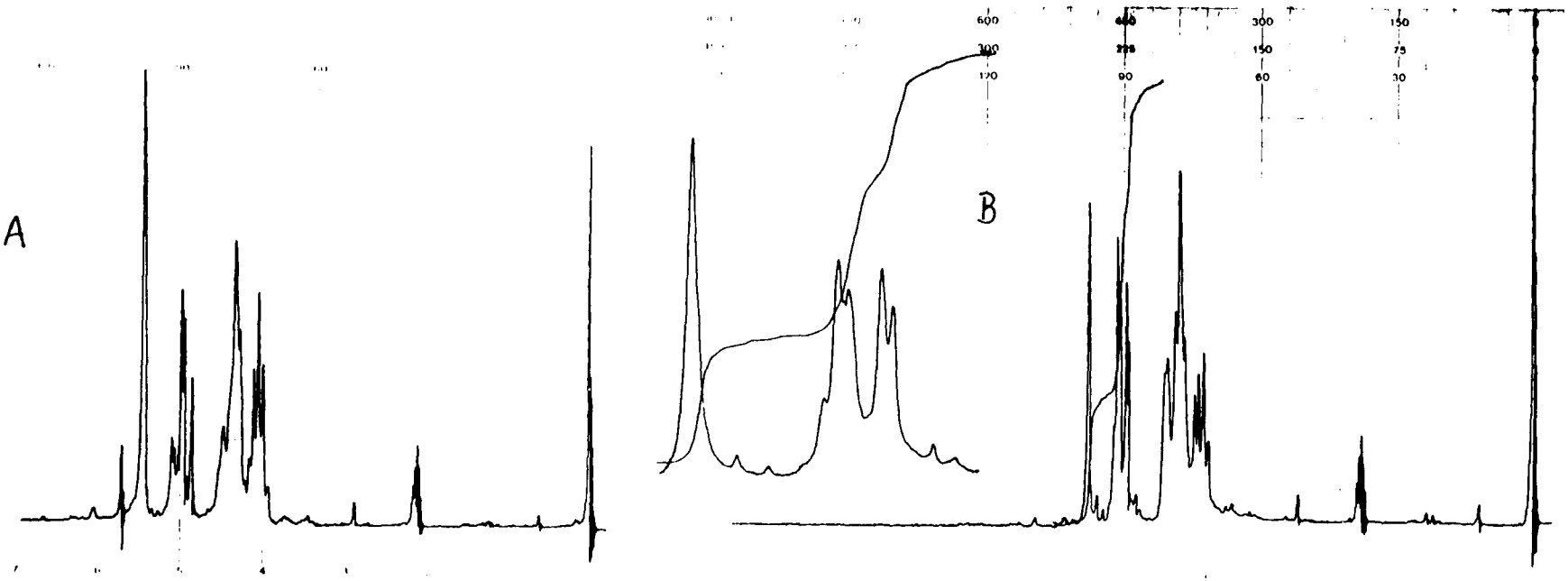


Fig. 10. ^{1}H-NMR Spectra of Copolyformals of Decafluoroheptanediol 6 and Tetranitrononanediol 8; A: 50/50; B: 80/20

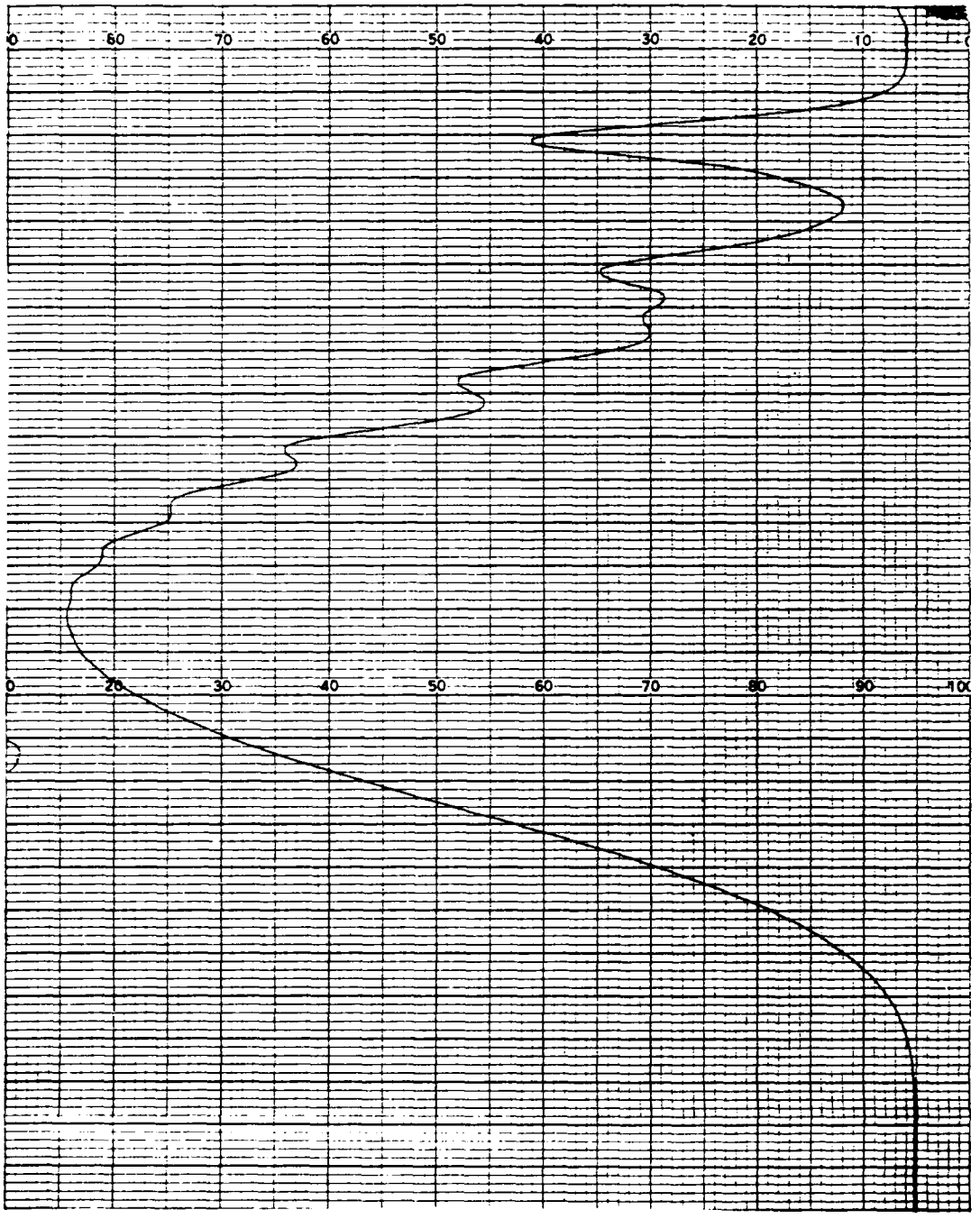


Fig. 11. GP Chromatogram of a Copolyformal of Hexanitropentadecanediol 10 and Decafluoroheptanediol 6 (Ratio 70/30; $\bar{M}_N$ = 2600)

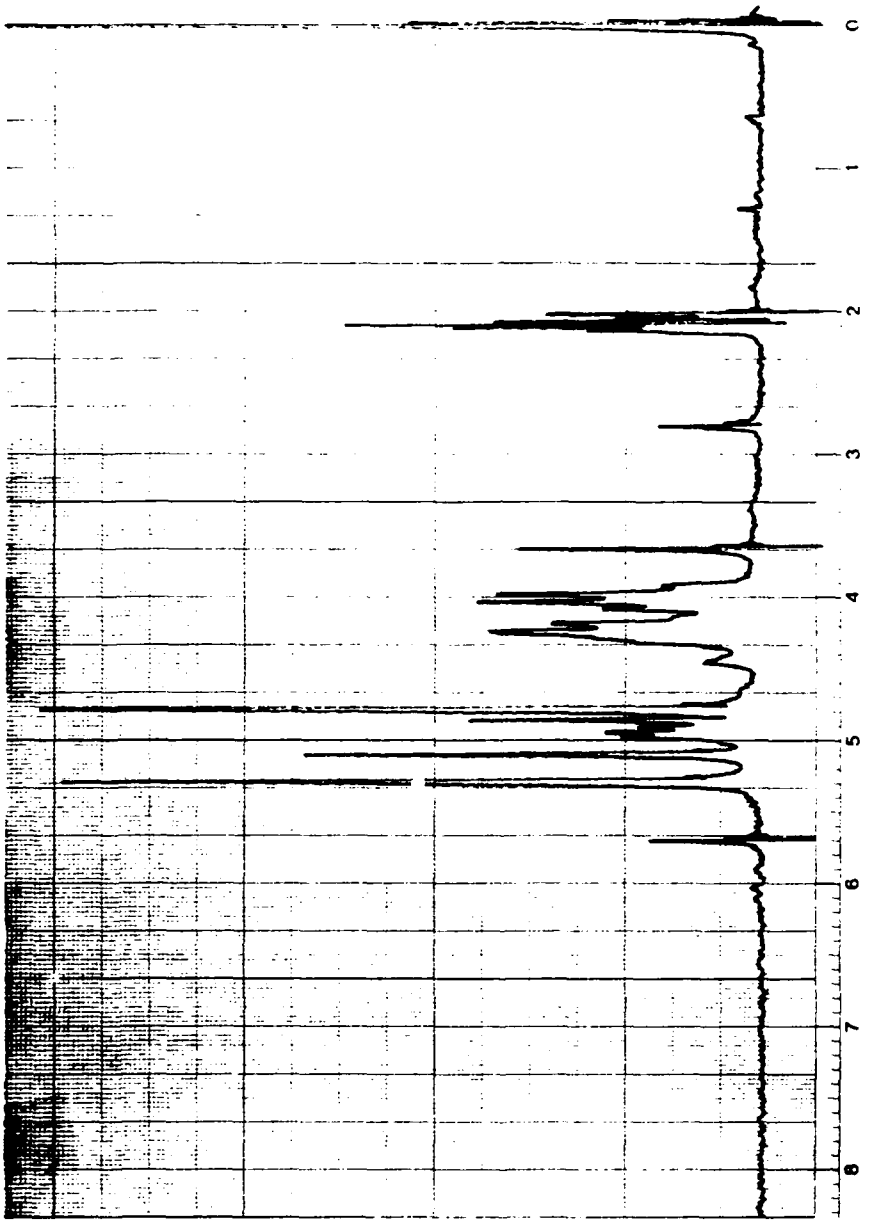


Fig. 12. ^{1}H-NMR Spectrum of a Copolyformal of Hexanitropentadecanediol 10 and Decafluoroheptanediol 6 (Ratio 70/30; $\bar{M}_N$ = 2600)

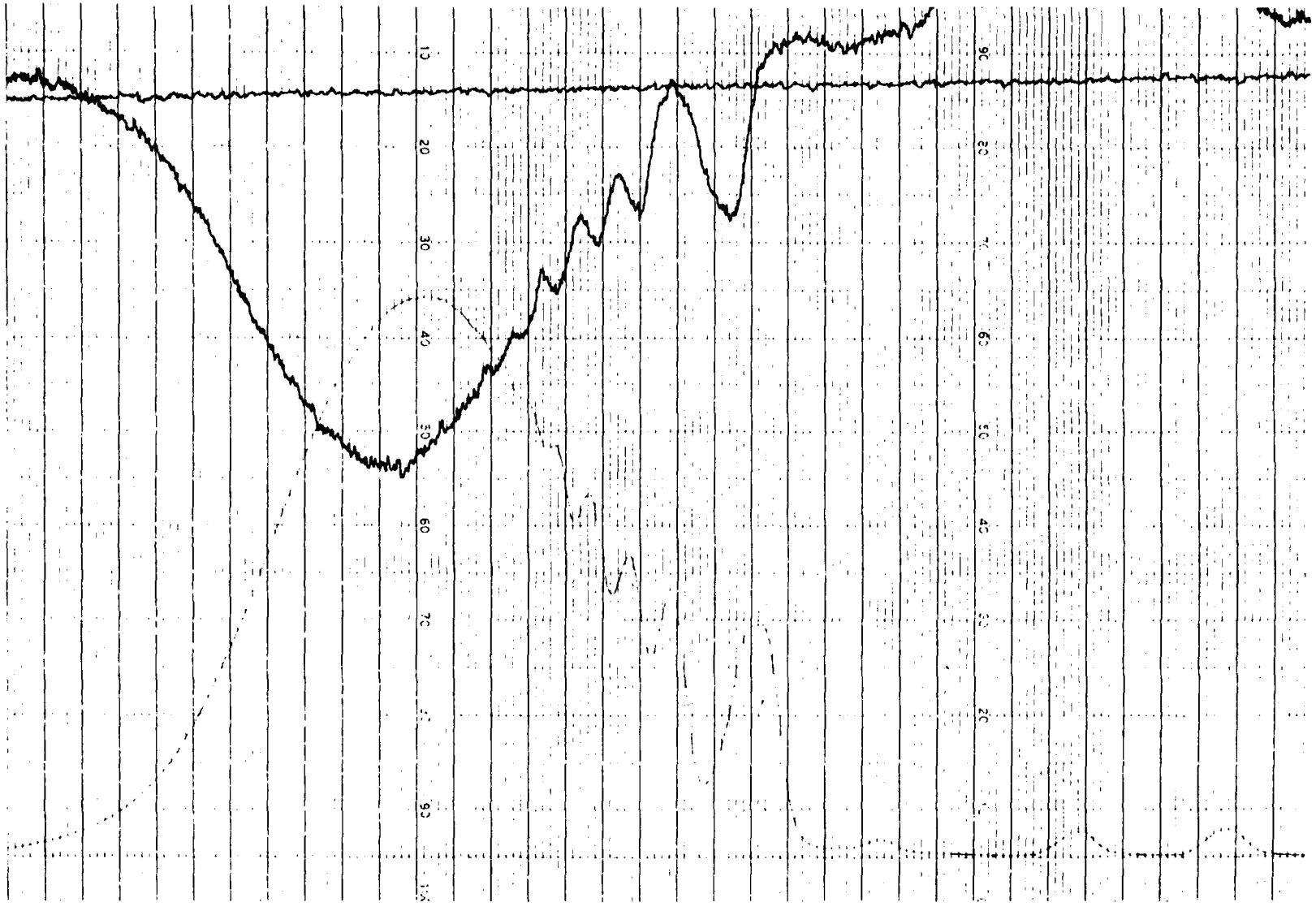


Fig. 13. GP Chromatogram of a Copolyformal of Hexanitropentadecanediol 10 and Octafluorohexanediol 5 (Ratio 70/30; $\bar{M}_N$ = 2000)

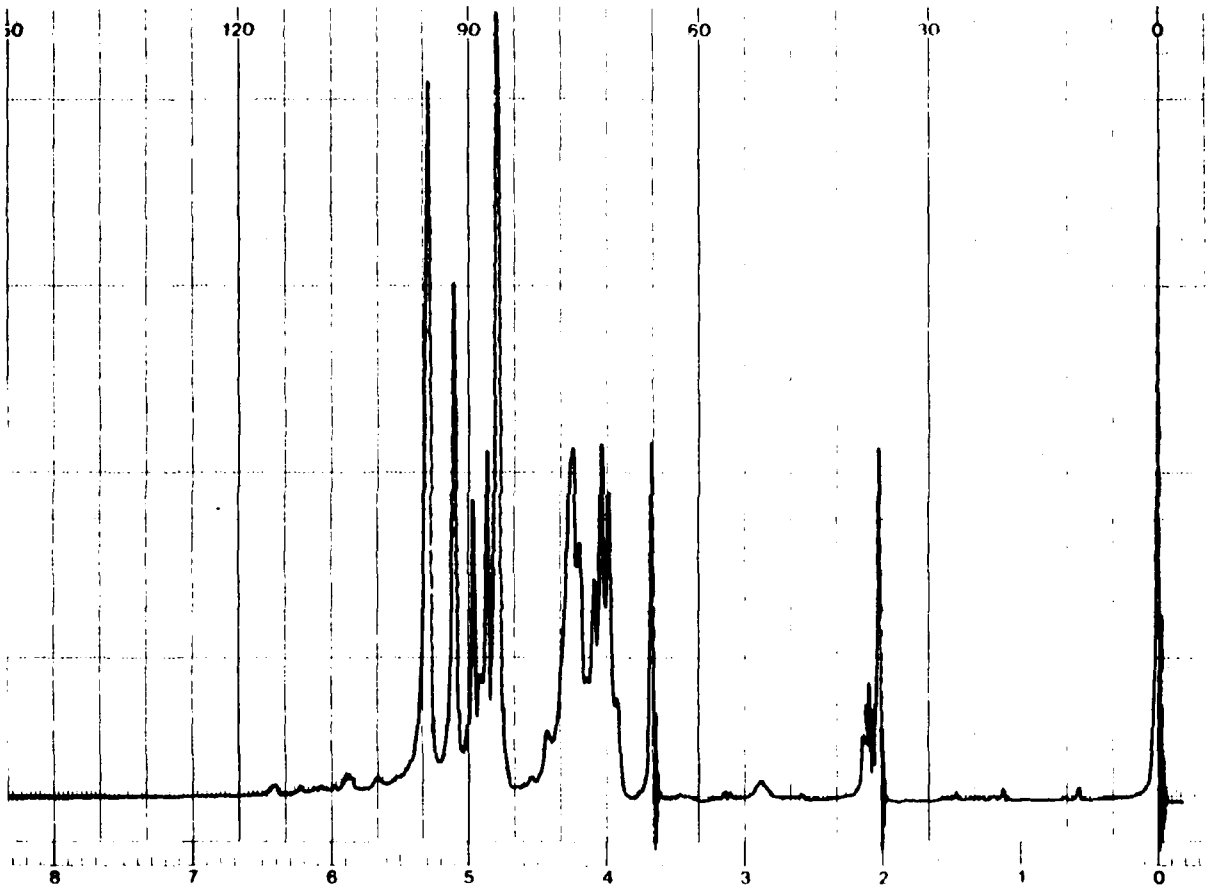


Fig. 14. ^{1}H-NMR Spectrum of a Copolyformal of Hexanitropentadecanediol 10 and Octafluorohexanediol 5 (Ratio 70/30; M_N = 2000)

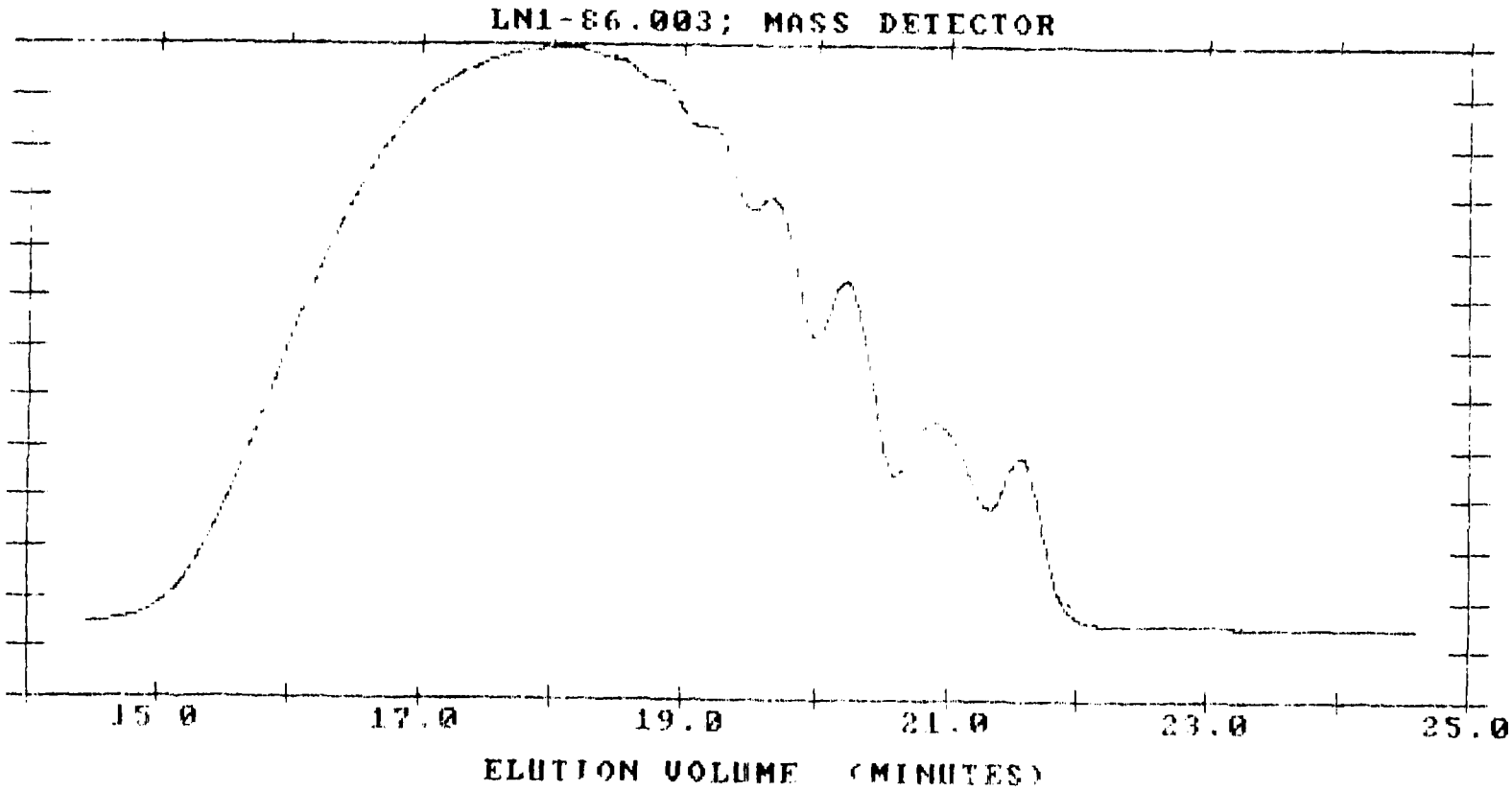


Fig. 15. GP Chromatogram of a Copolyformal of Octafluorohexanediol 5 and bis(hydroxyethyl)-o-carborane (65:35)

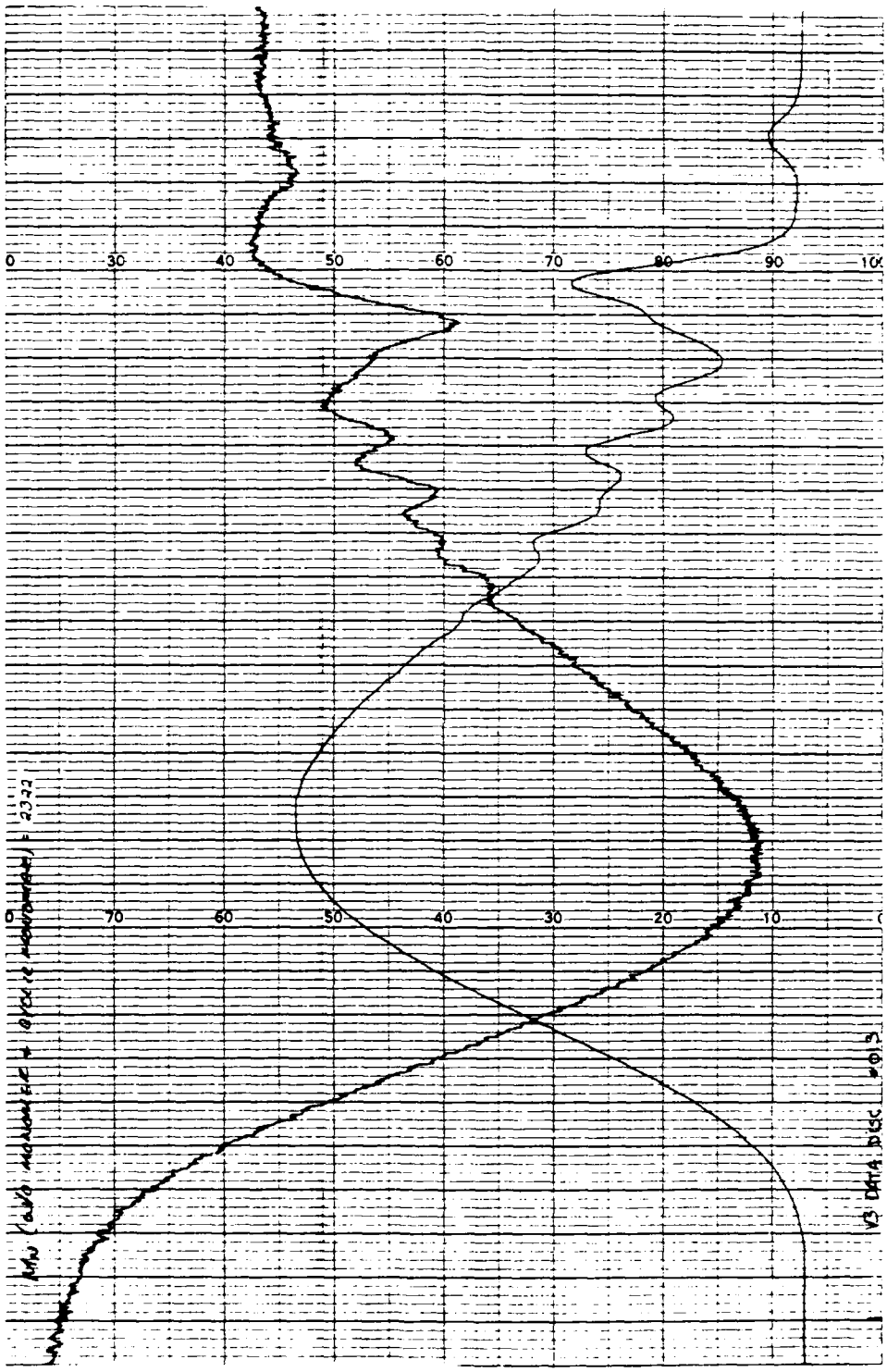


Fig 16. GP Chromatogram of a Copolyformal of Hexanitropentadecanediol 10 and bis(hydroxyethyl)-o-carborane (70:30)

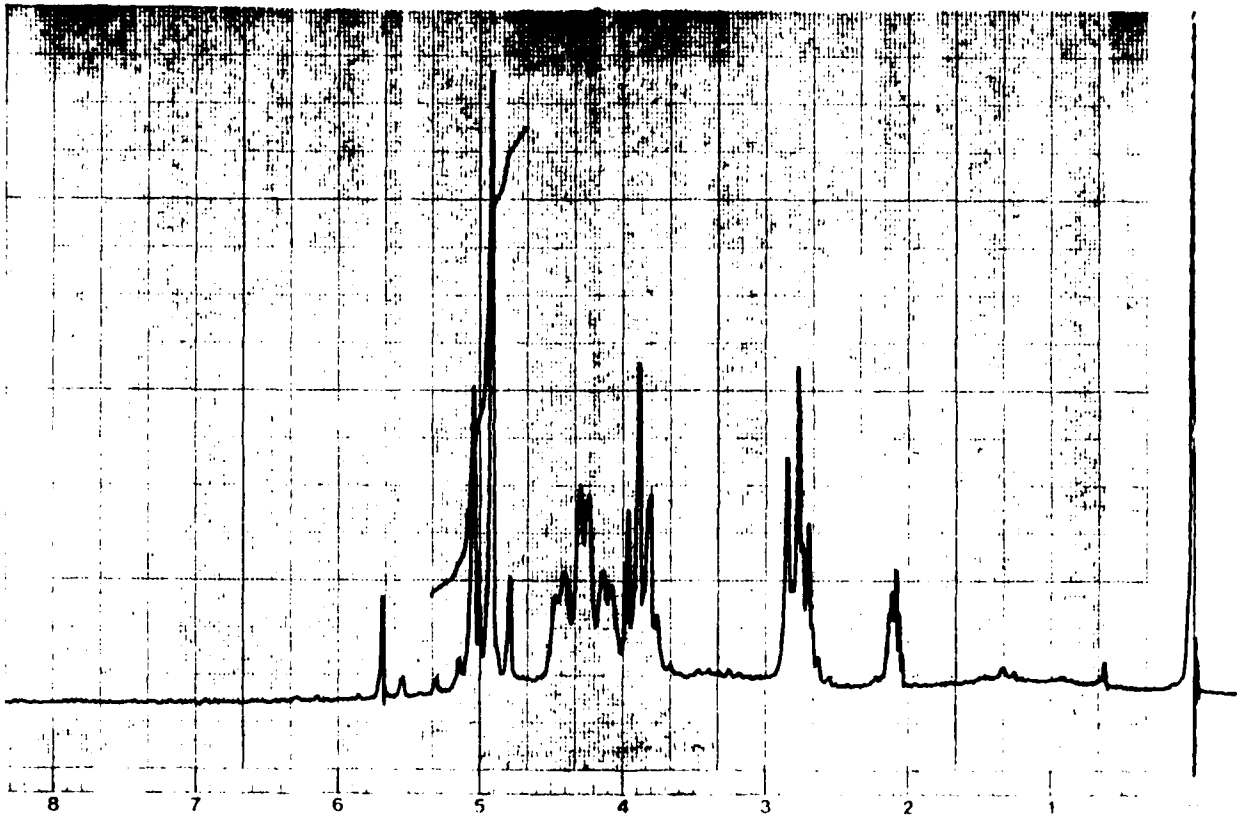


Fig. 17. ^{1}H-NMR Spectrum of a Copolyformal of Octafluorohexanediol 5 and bis(hydroxyethyl)-o-carborane (65:35)

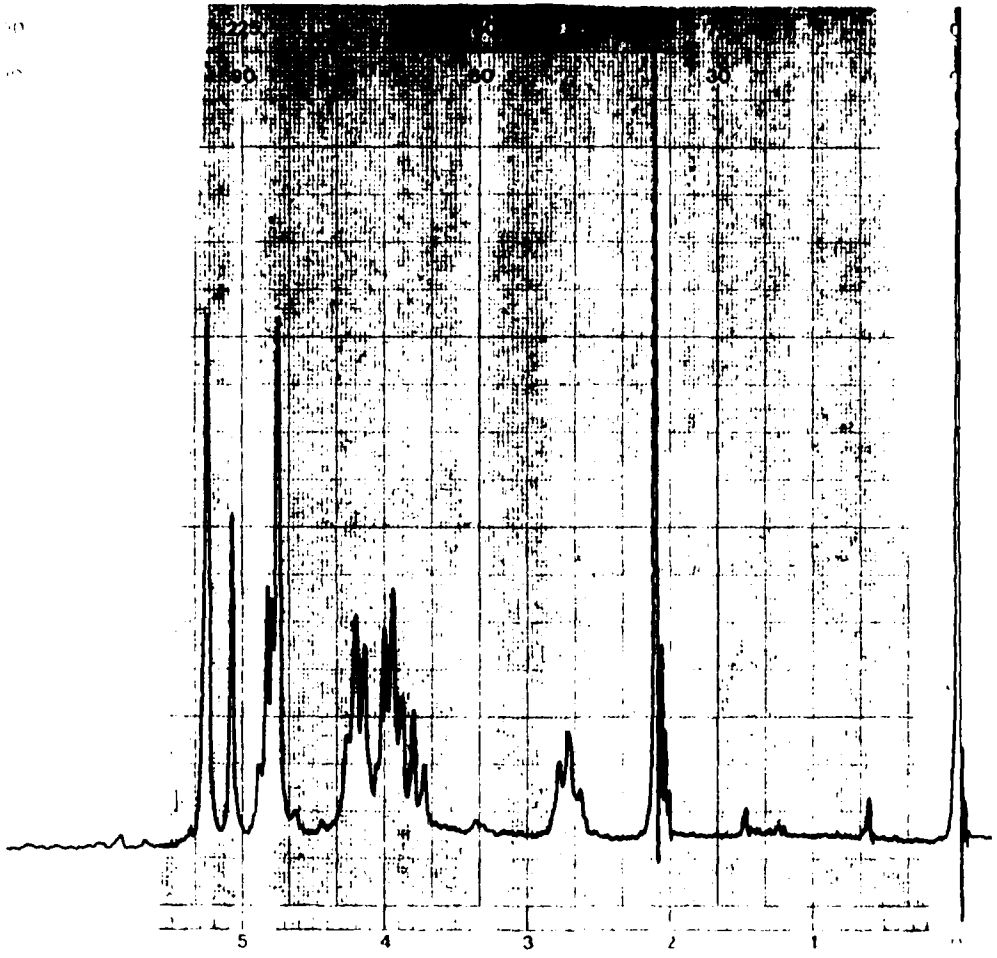


Fig. 18. ^{1}H-NMR Spectrum of a Copolyformal of Hexanitropentadecanediol 10 and bis(hydroxyethyl)-o-carborane (70:30)

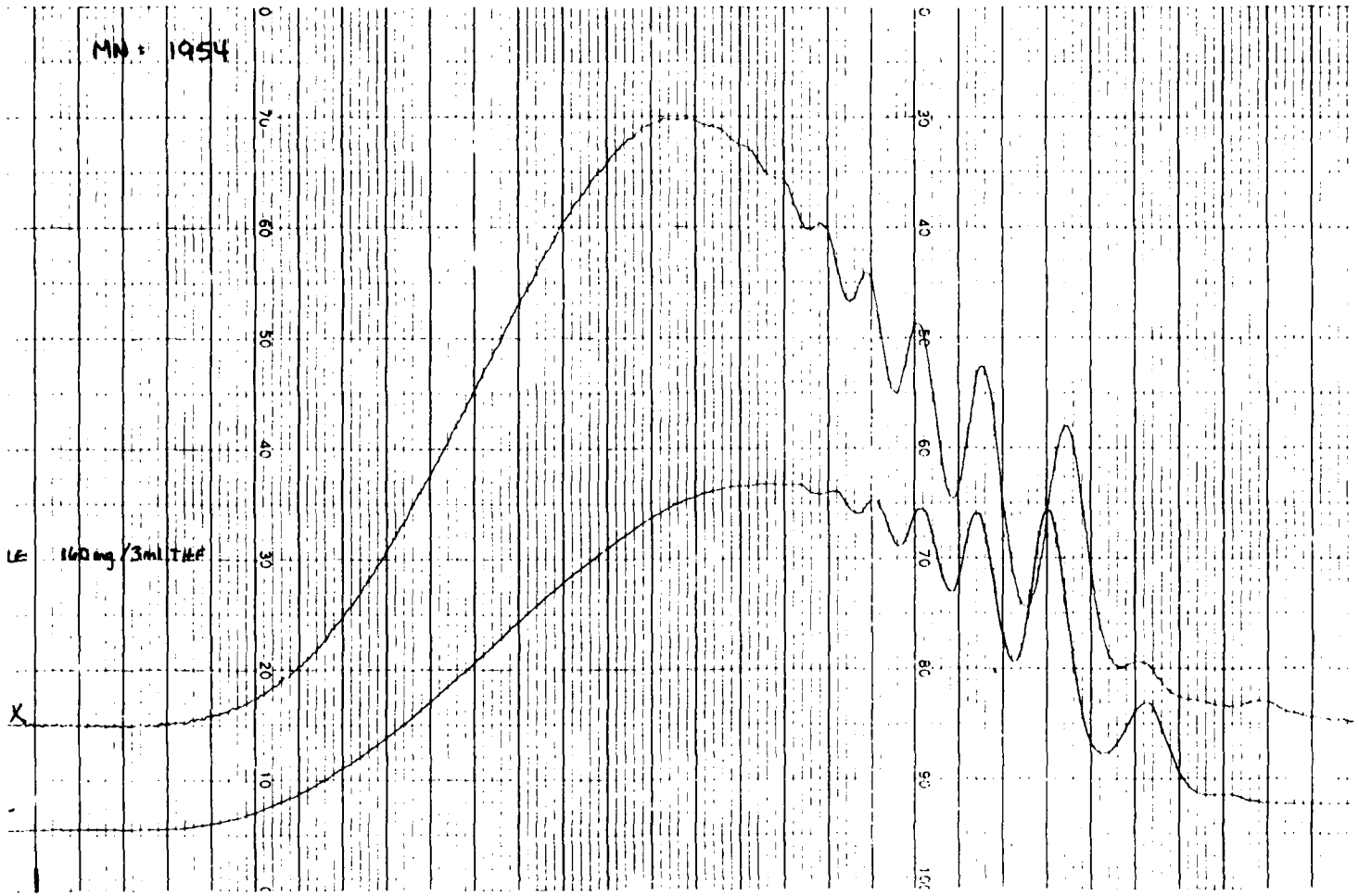


Fig. 19. GP Chromatogram of a Copolyformal of Decafluorodiol 6 and Nitrazapentanediol 11 (97.5:2.5)

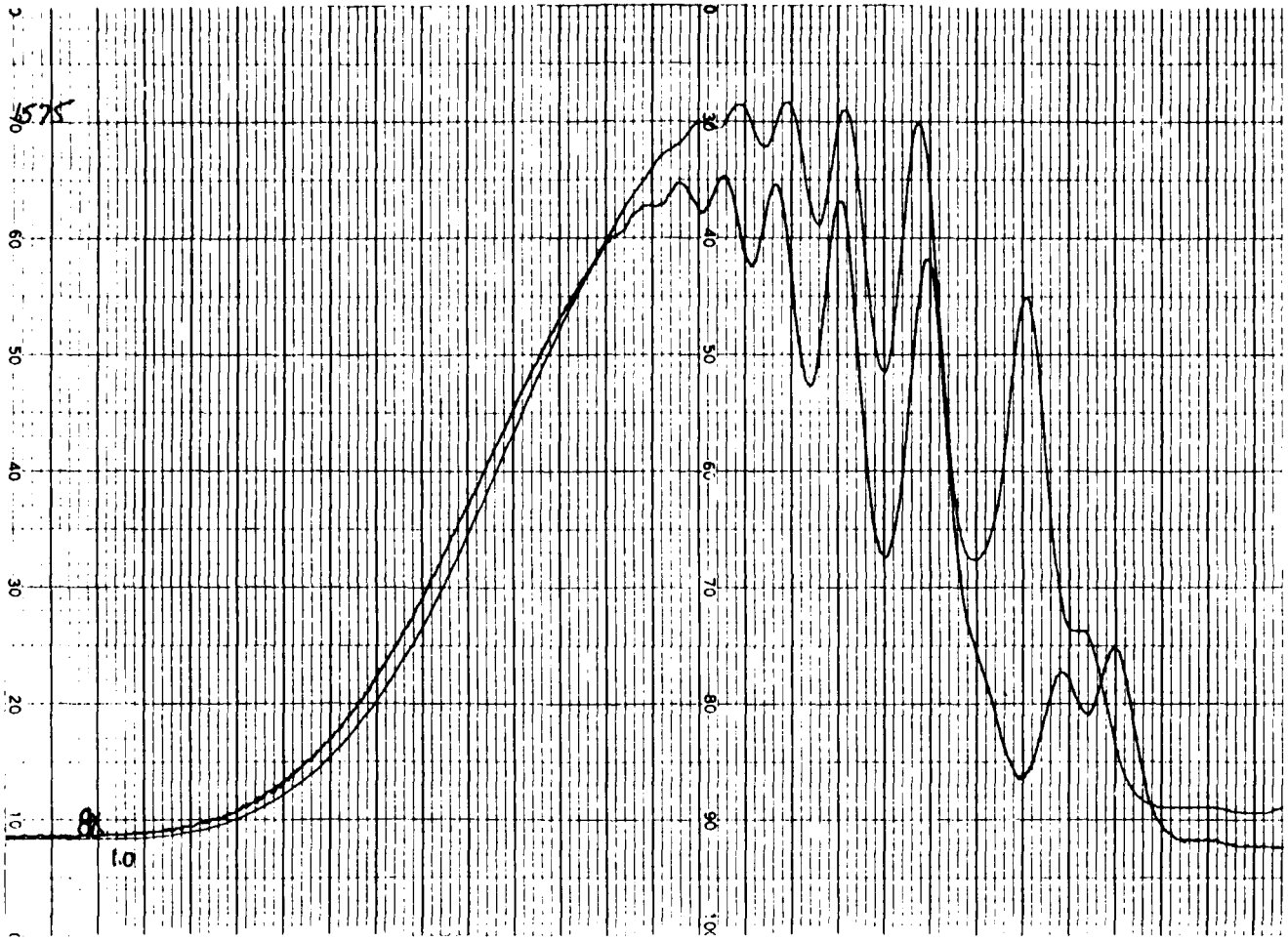


Fig. 20. GP Chromatogram of a Copolyformal of Decafluorodiol 6 and Nitrazapentanediol 11 (90:10)

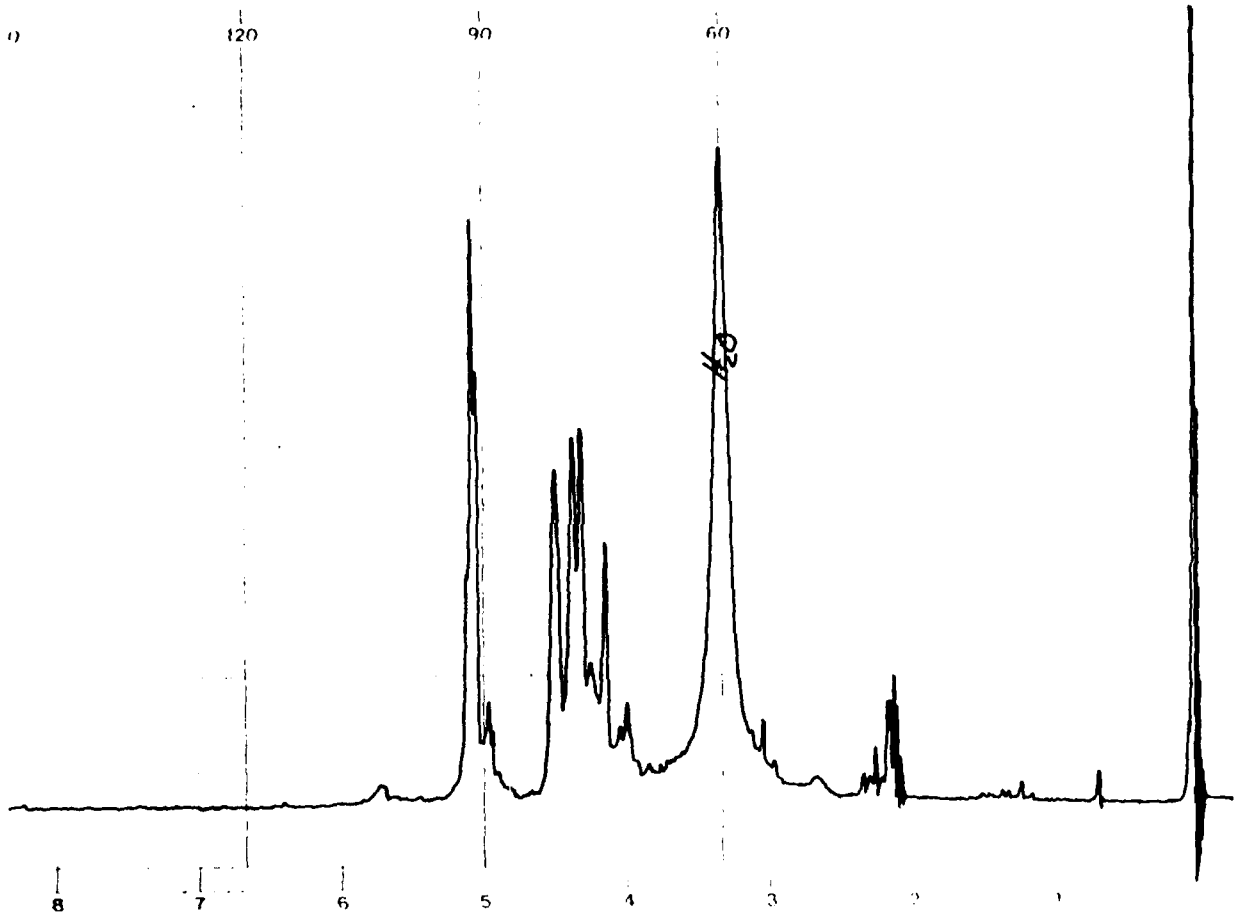


Fig. 21. ^{1}H-NMR Spectrum of a Copolyformal of Decafluorodiol 6 and Nitrazapentanediol 11 (90:10)

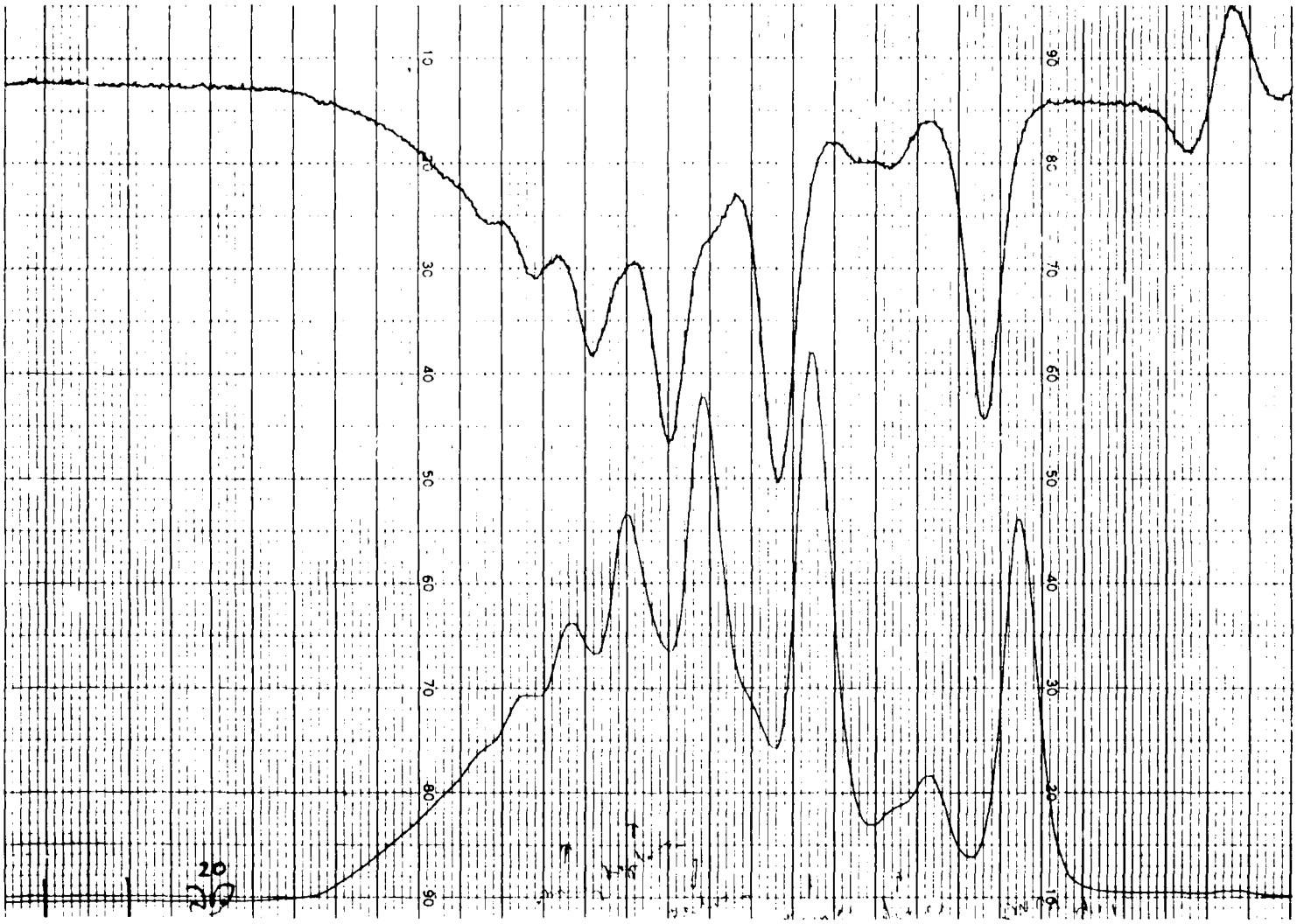


Fig. 22. GP Chromatogram of Oligomers from Tetranitrononanediol 13 and 4,4-Dinitropimeloyl Chloride (1:2)

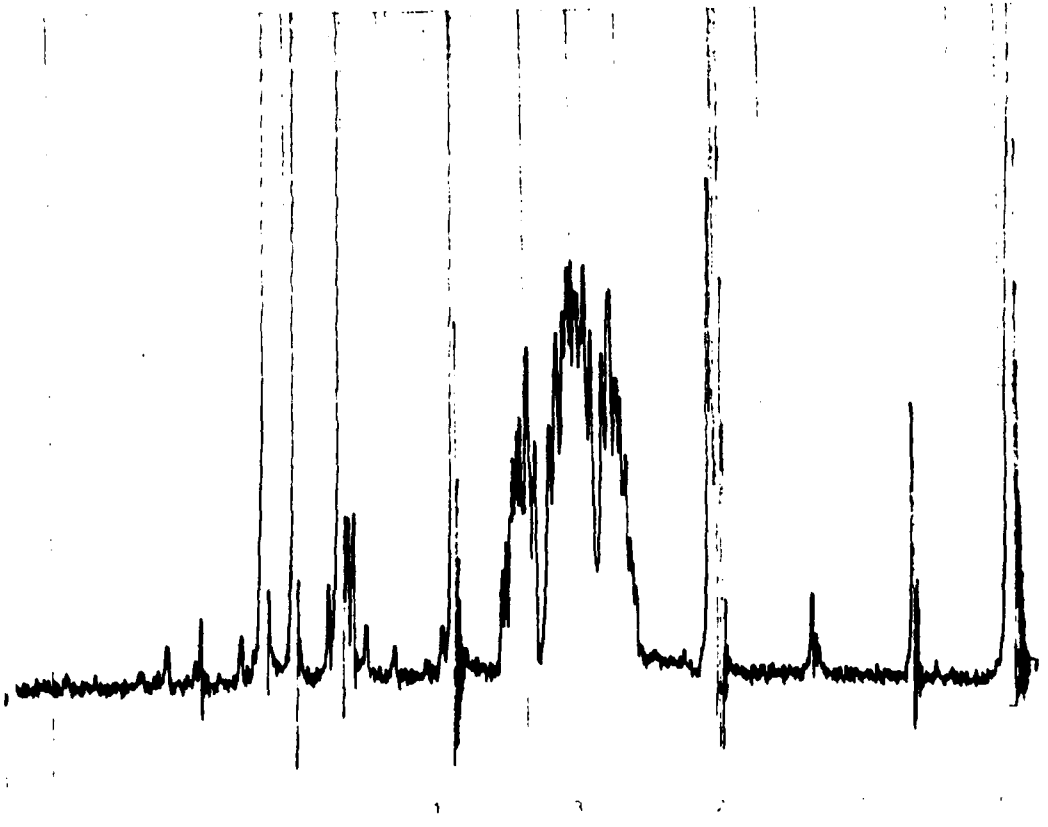


Fig. 23. ^{1}H-NMR Spectrum of Oligomers from Tetranitrononanediol 13 and 4,4-Dinitropimeloyl Chloride (1:2)

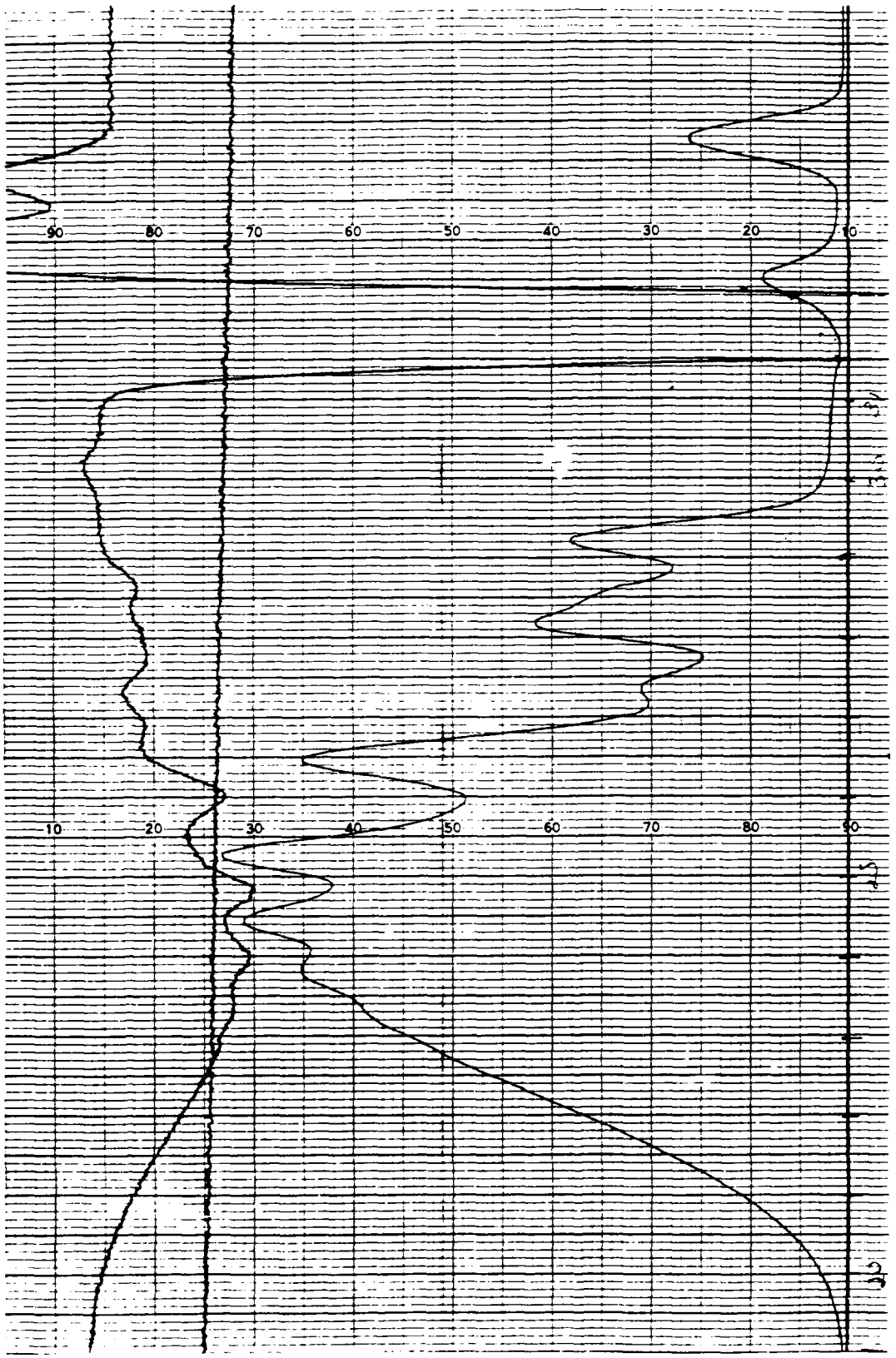


Fig. 24. GP Chromatogram of Oligomers in Fig. 22 after Reaction with Trifluoroethanol

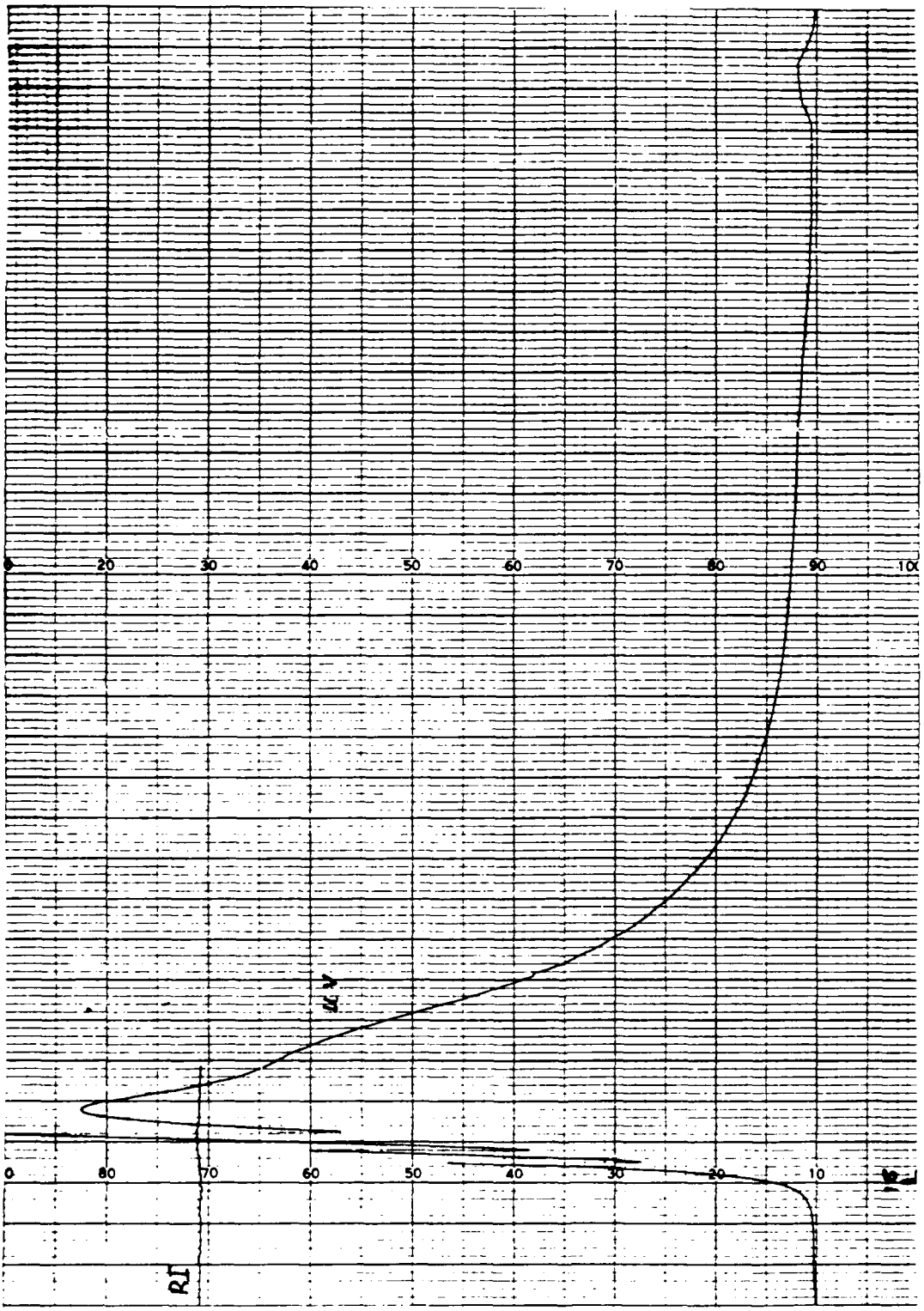


Fig. 25. GP Chromatogram of a Block Copolymer of FPF-1 ($\bar{M}_N$ = 5450) End-capped with TDI and Chain-extended with Dinitrazaoctanediol 7 (1:0.8)

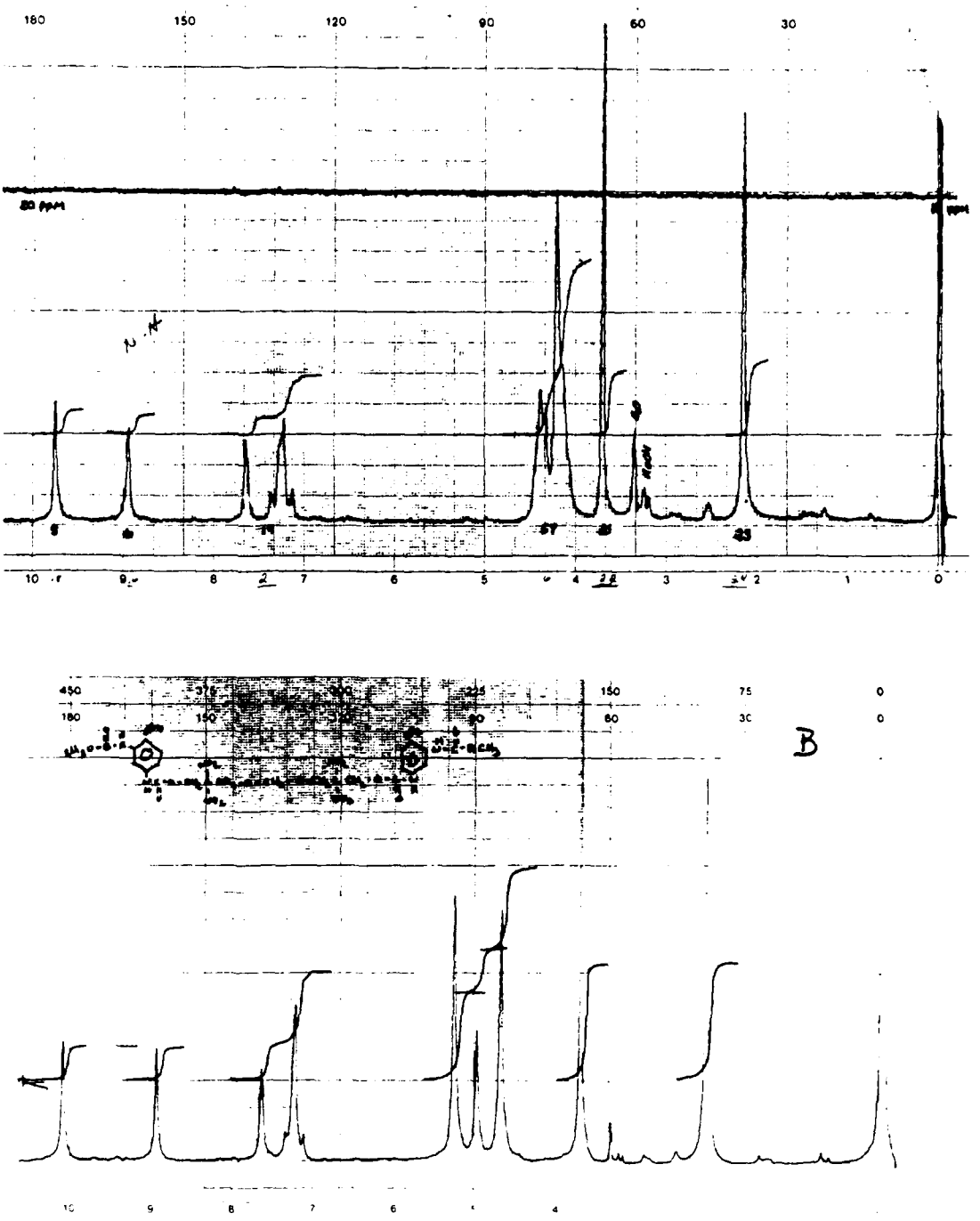


Fig. 26. ^{1}H-NMR Spectra of Diurethanes from Reaction of (A) 15 and (B) 16 with Excess Methanol

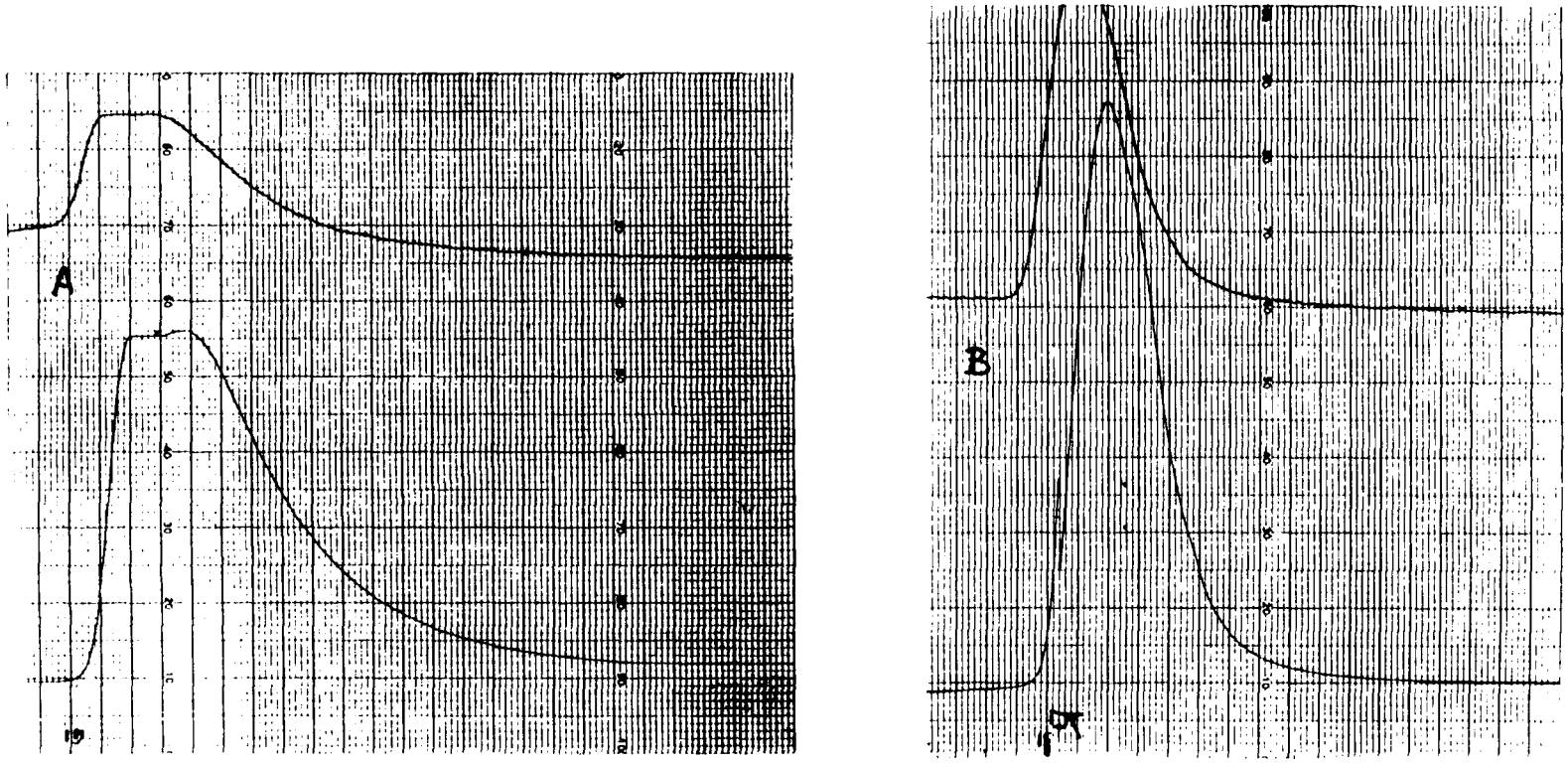


Fig. 27. GP Chromatogram of FPF-1 Chain-extended with 2-Nitrazapropane Diisocyanate; (A): FPF-1 $\bar{M}_N$ = 2150; (B): FPF-1 $\bar{M}_N$ = 5450

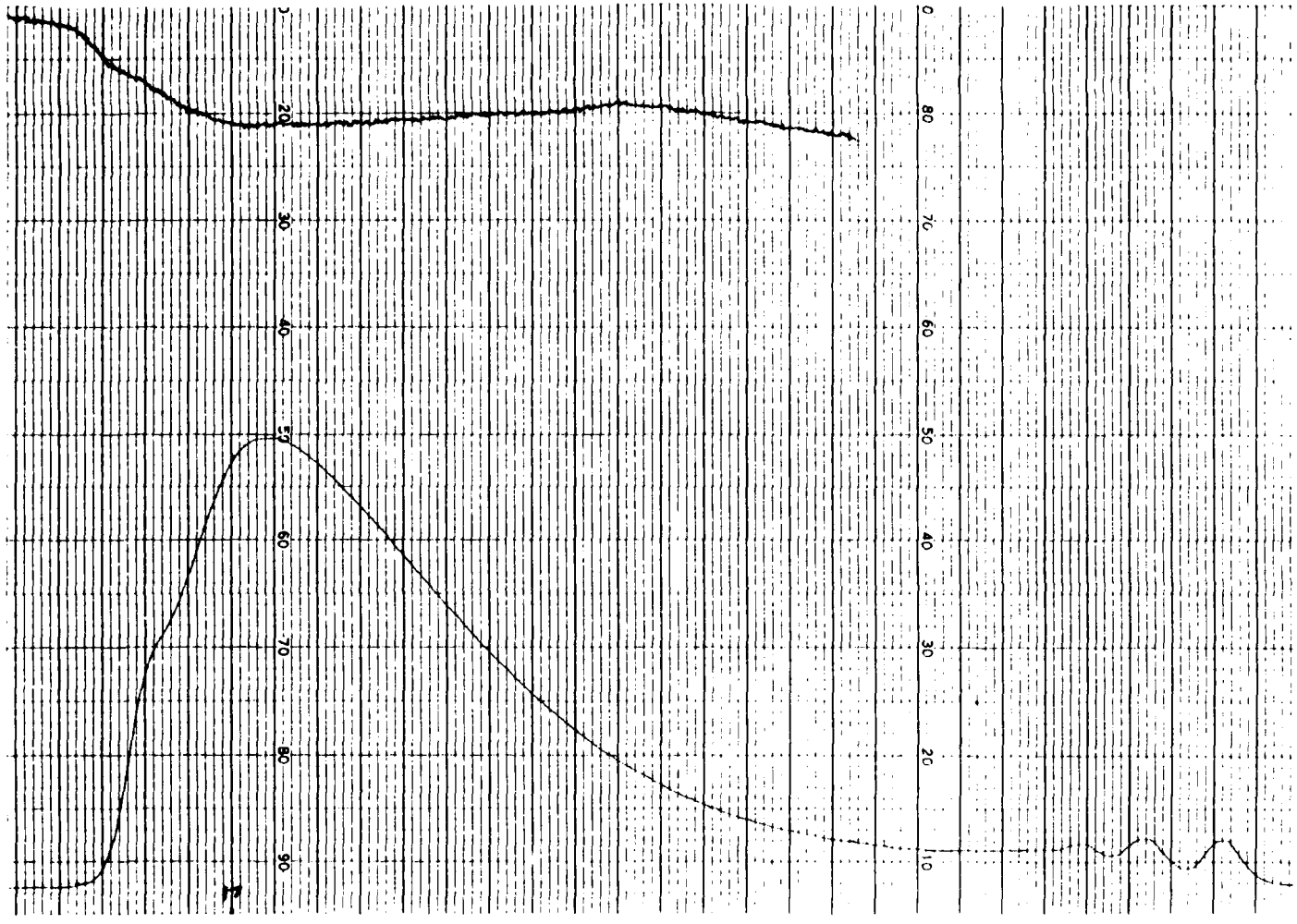


Fig. 28. GP Chromatogram of a 5-Co-7 Polyformal (50:50) Chain-extended with 3,3-Dinitropentane Diisocyanate

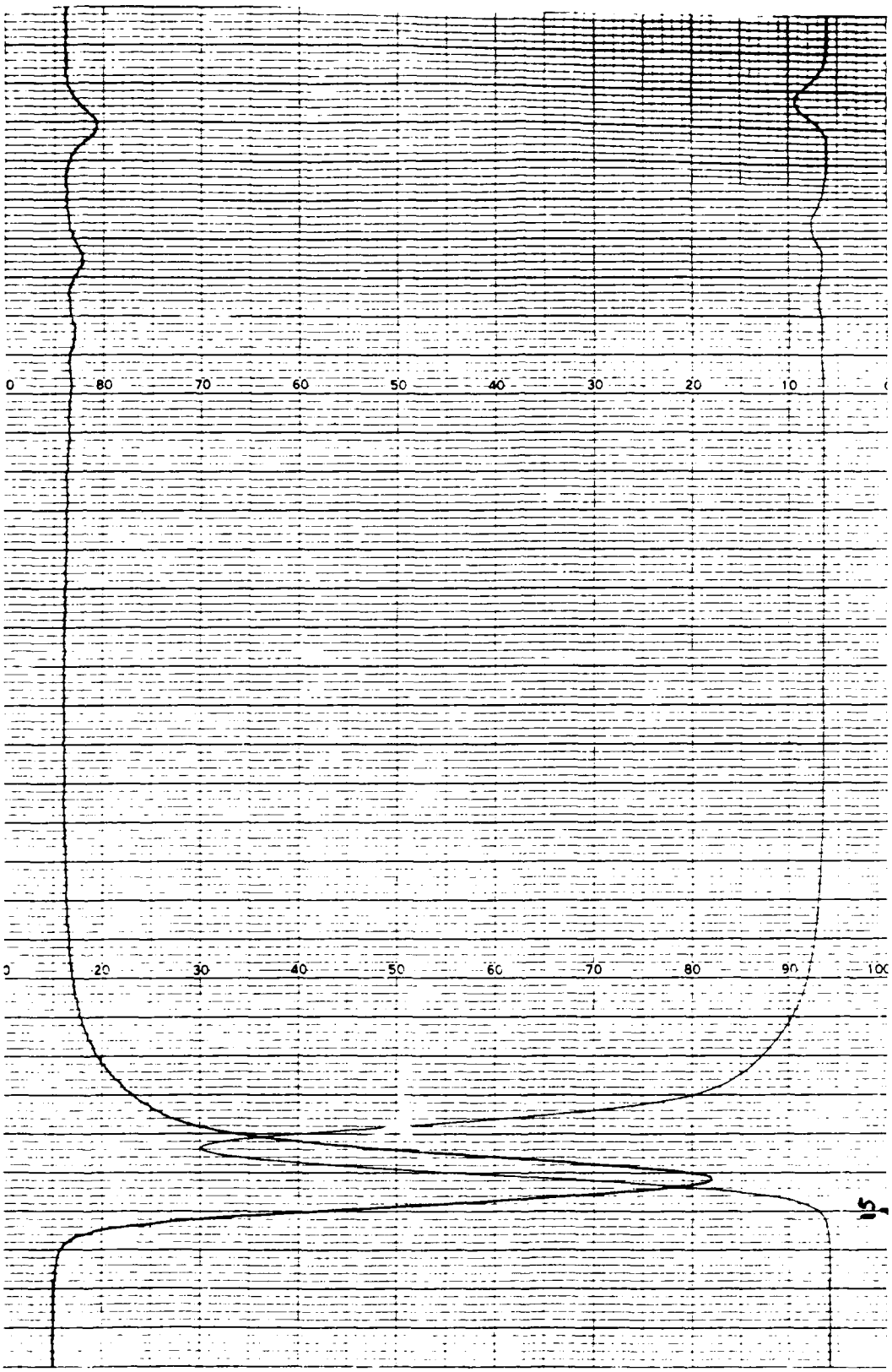


Fig. 29. GP Chromatogram of a Polyformal of Tetranitrotridecanediol 9, Chain-extended with 3,3-Dinitropentane Diisocyanate

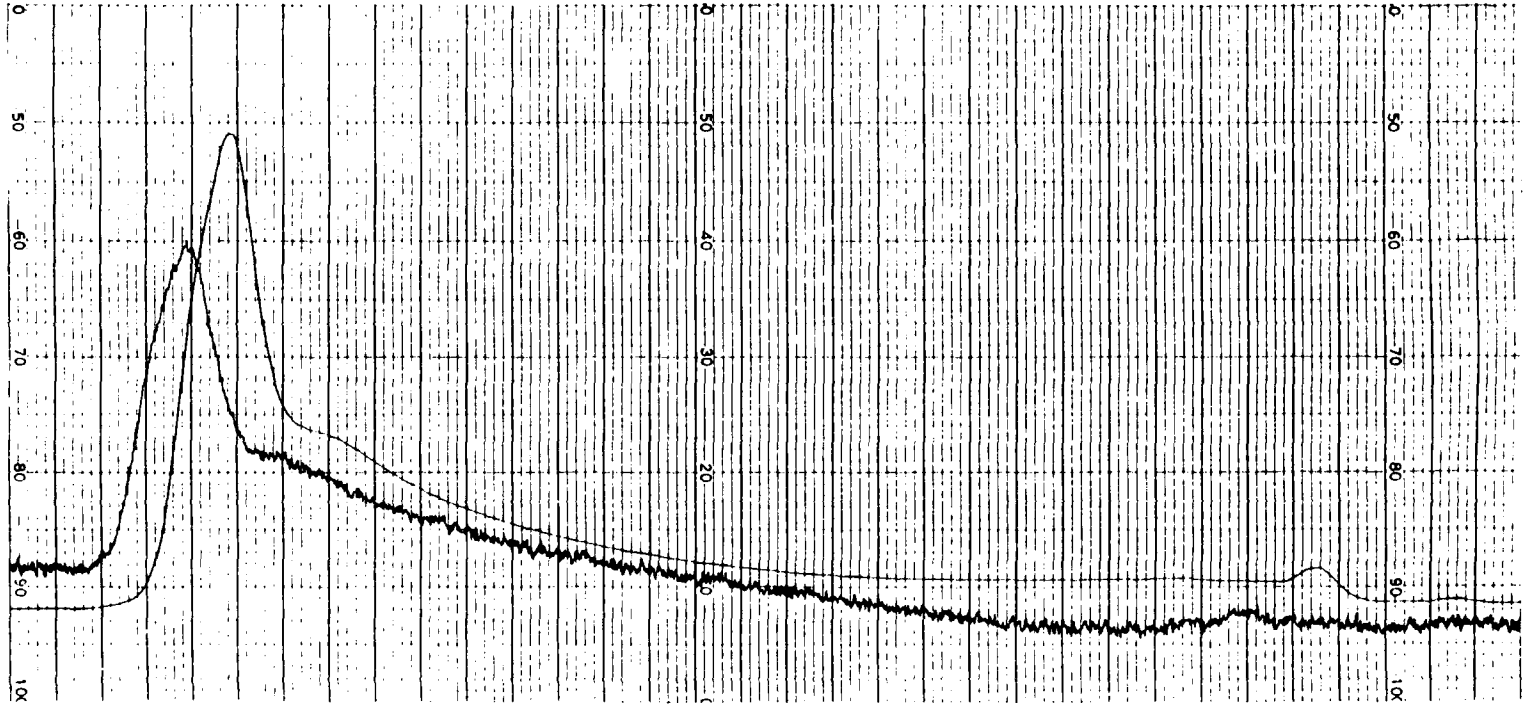


Fig. 30. GP Chromatogram of a Polymer Prepared by Chain-extension of a Polyformal of Decafluorodiol 6 ($\bar{M}_N \simeq 3300$) with Toluene-2,4-diisocyanate

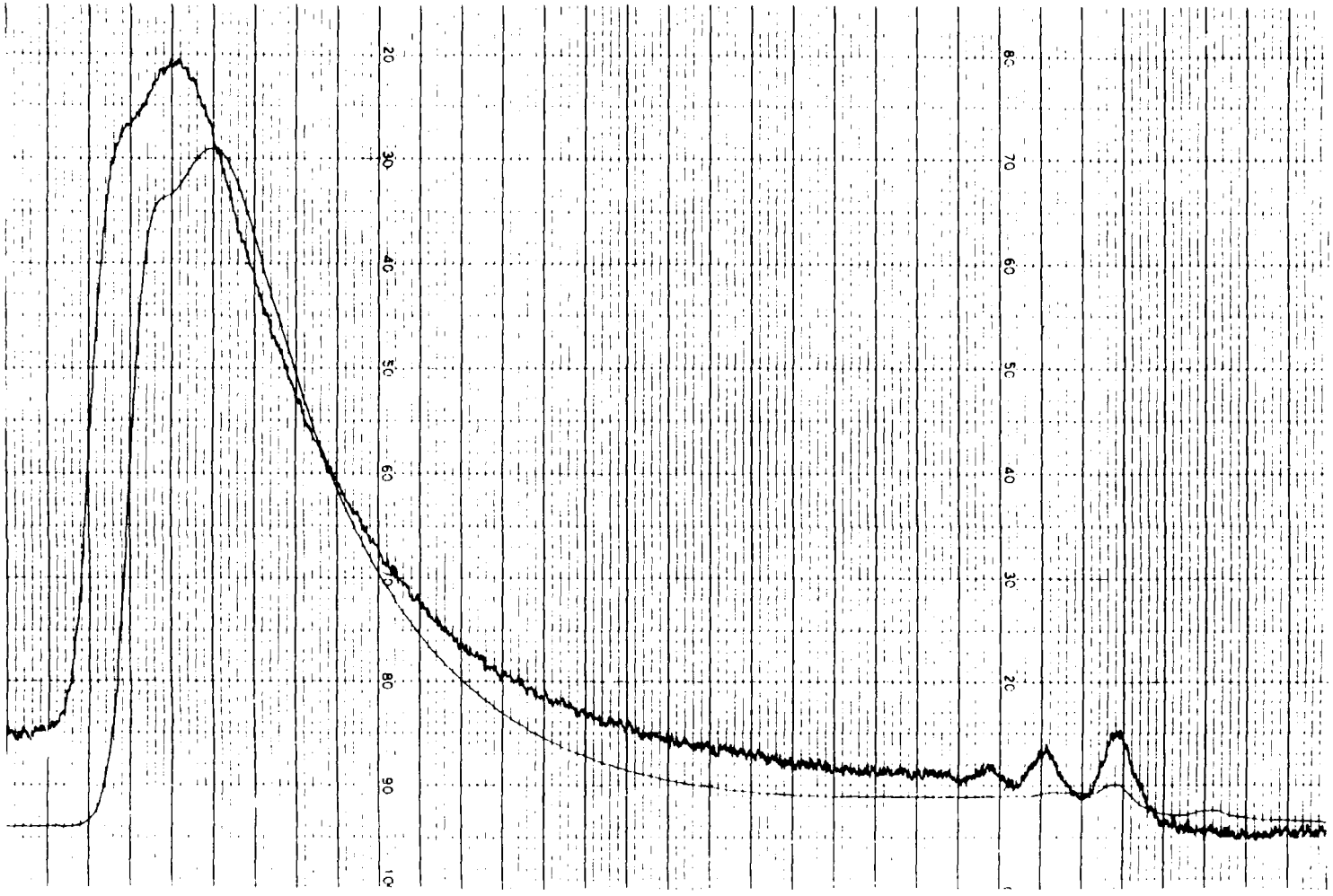


Fig. 31. GP Chromatogram of a Polymer Prepared by Chain-extension of a Polyformal of Octafluorotriethylene Glycol ($\bar{M}_N \simeq 2700$) with Toluene-2,4-diisocyanate

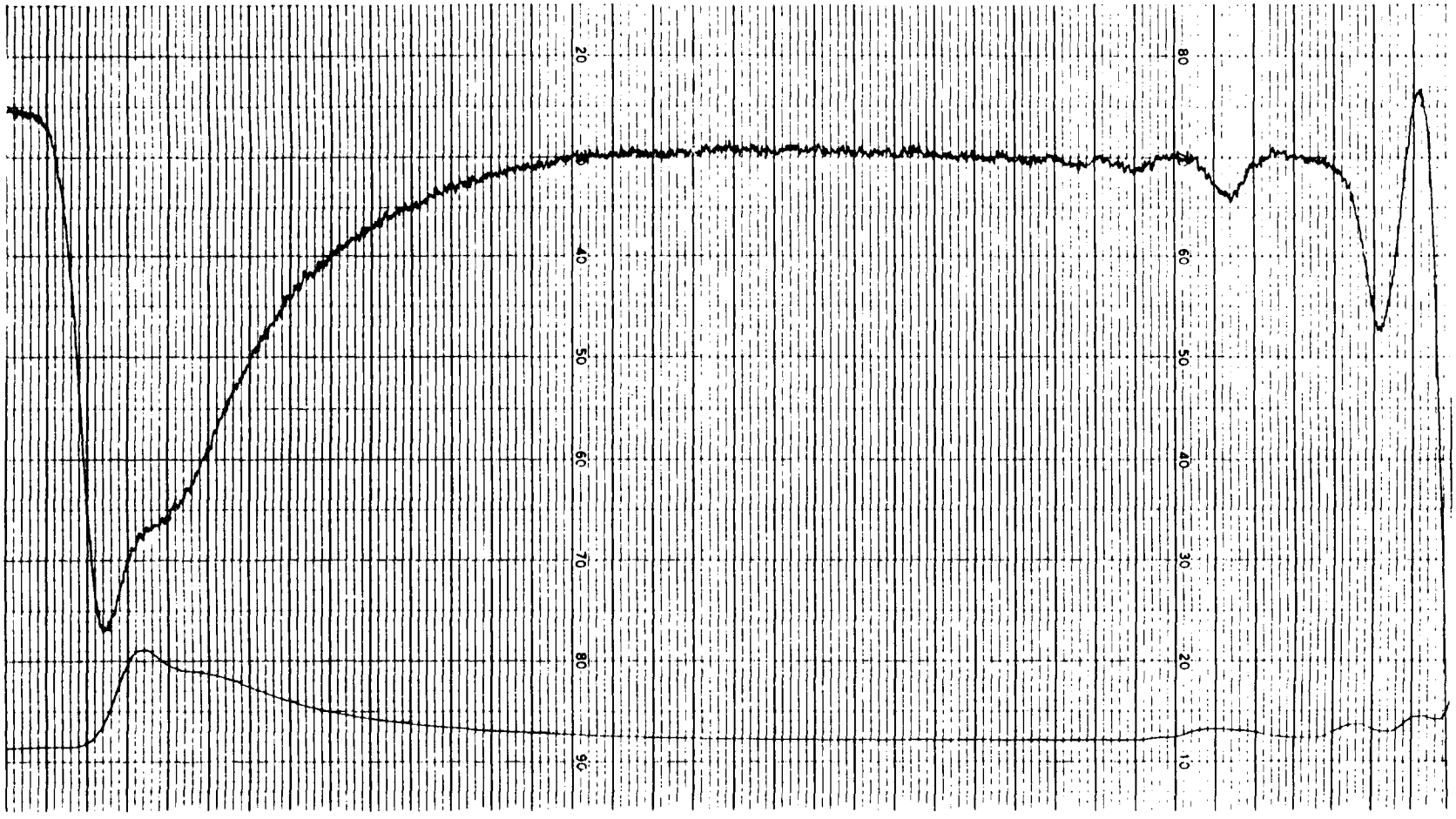


Fig. 32. GP Chromatogram of a Polymer Prepared by Chain-extension of Poly(2-Butoxydioxepane) with 3,3-Dinitropentane-1,5-diisocyanate

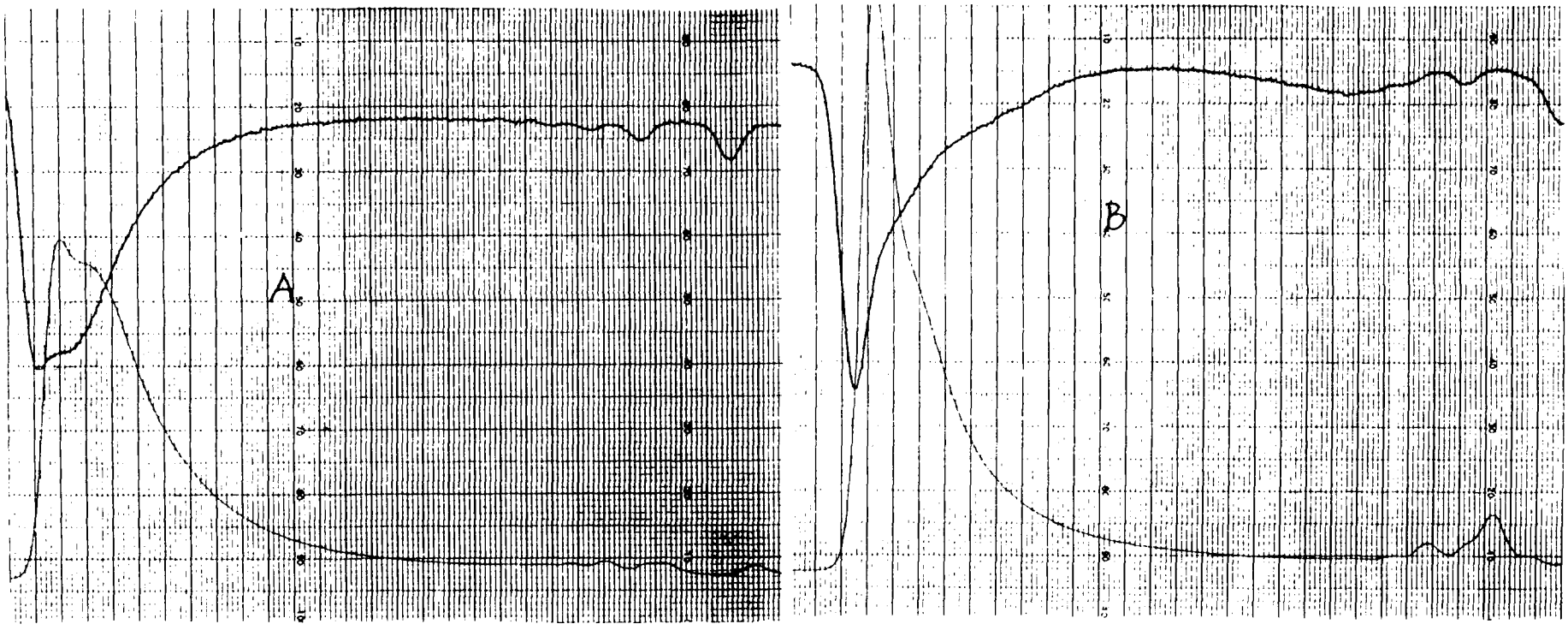


Fig. 33. GP Chromatogram of a Polymer Prepared by Chain-extension of a Polyformal of Tetranitrotridecanediol 9 with 15; (A): $\bar{M}_N$ of 9 Polyformal = 4460; (B): $\bar{M}_N$ = 7600

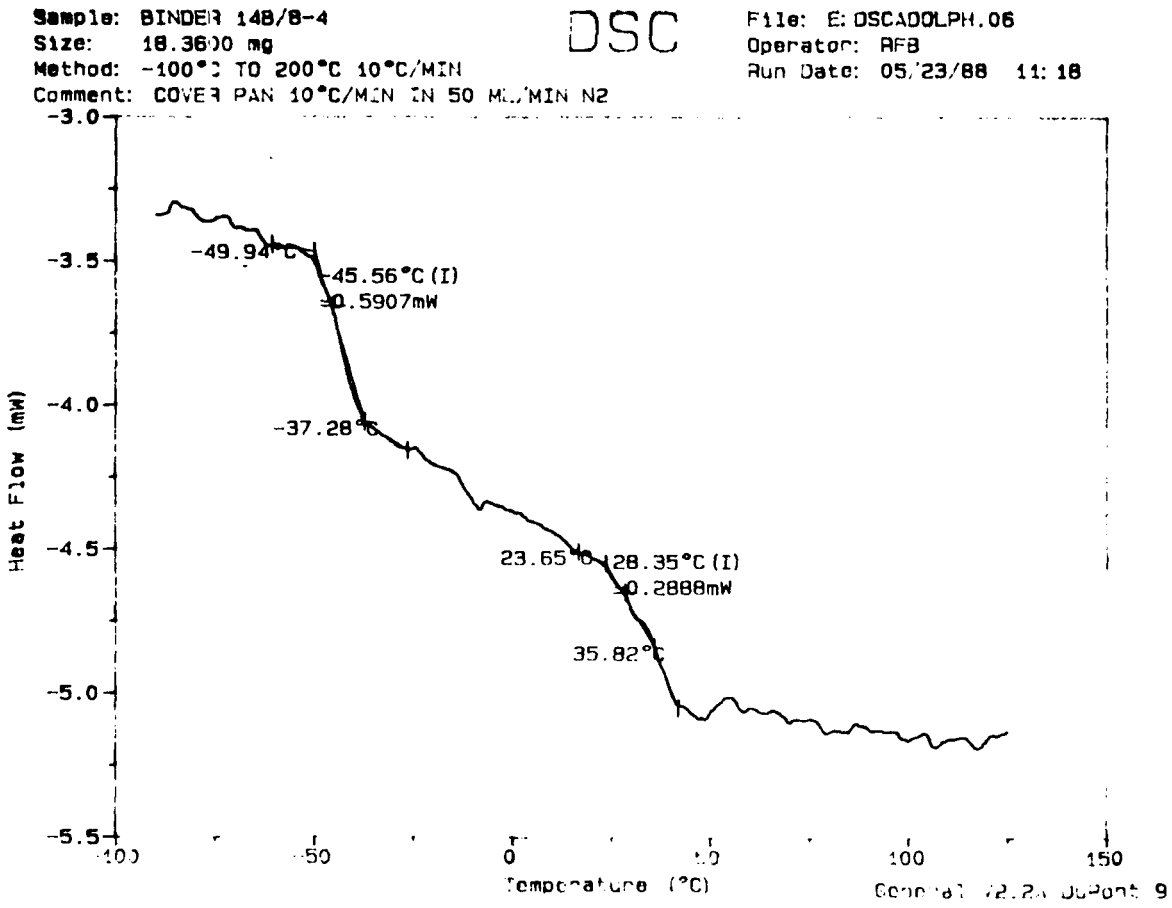


Fig. 34. DSC Curve of FPF-1 (5400)/TDI/Tetranitrodiazanonanediol polyformal Block Copolymer

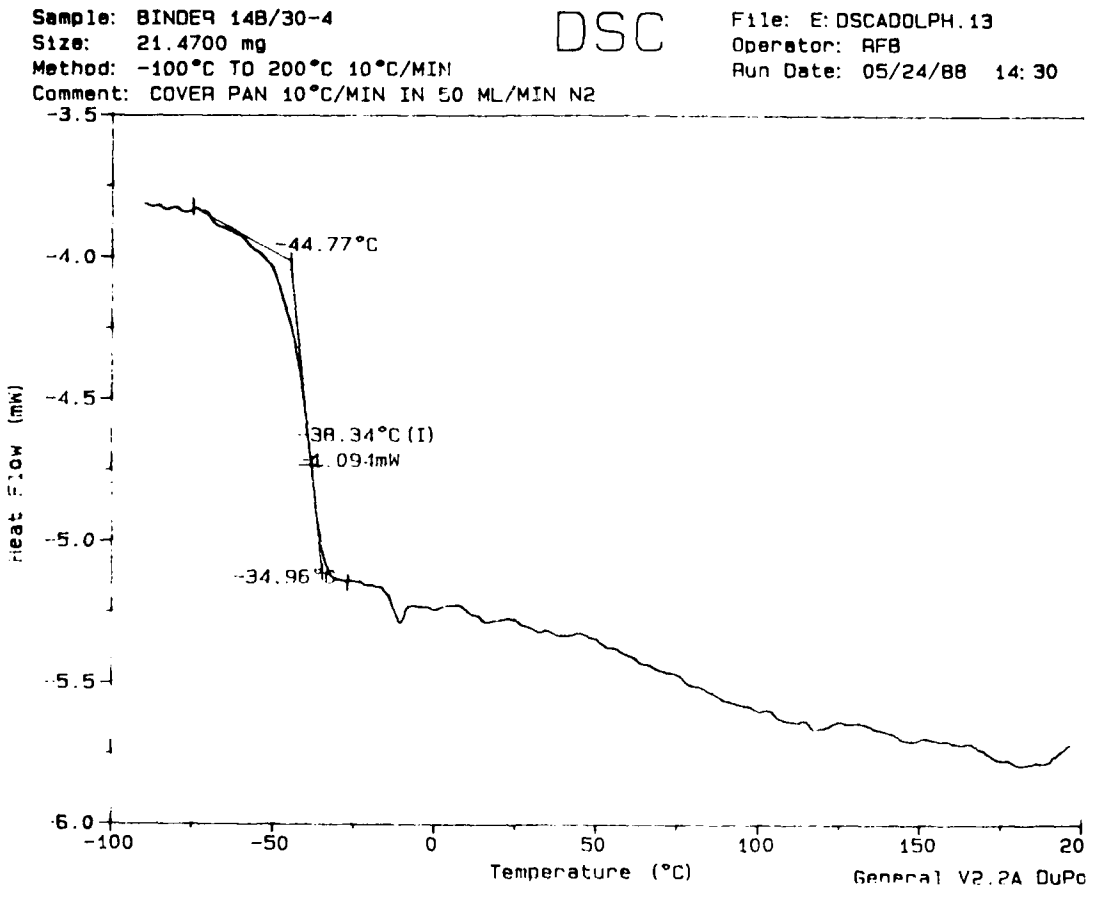


Fig. 35. DSC Curve of FPF-1 (5400)/2-Nitrazapropane Diisocyanate Block Copolymer

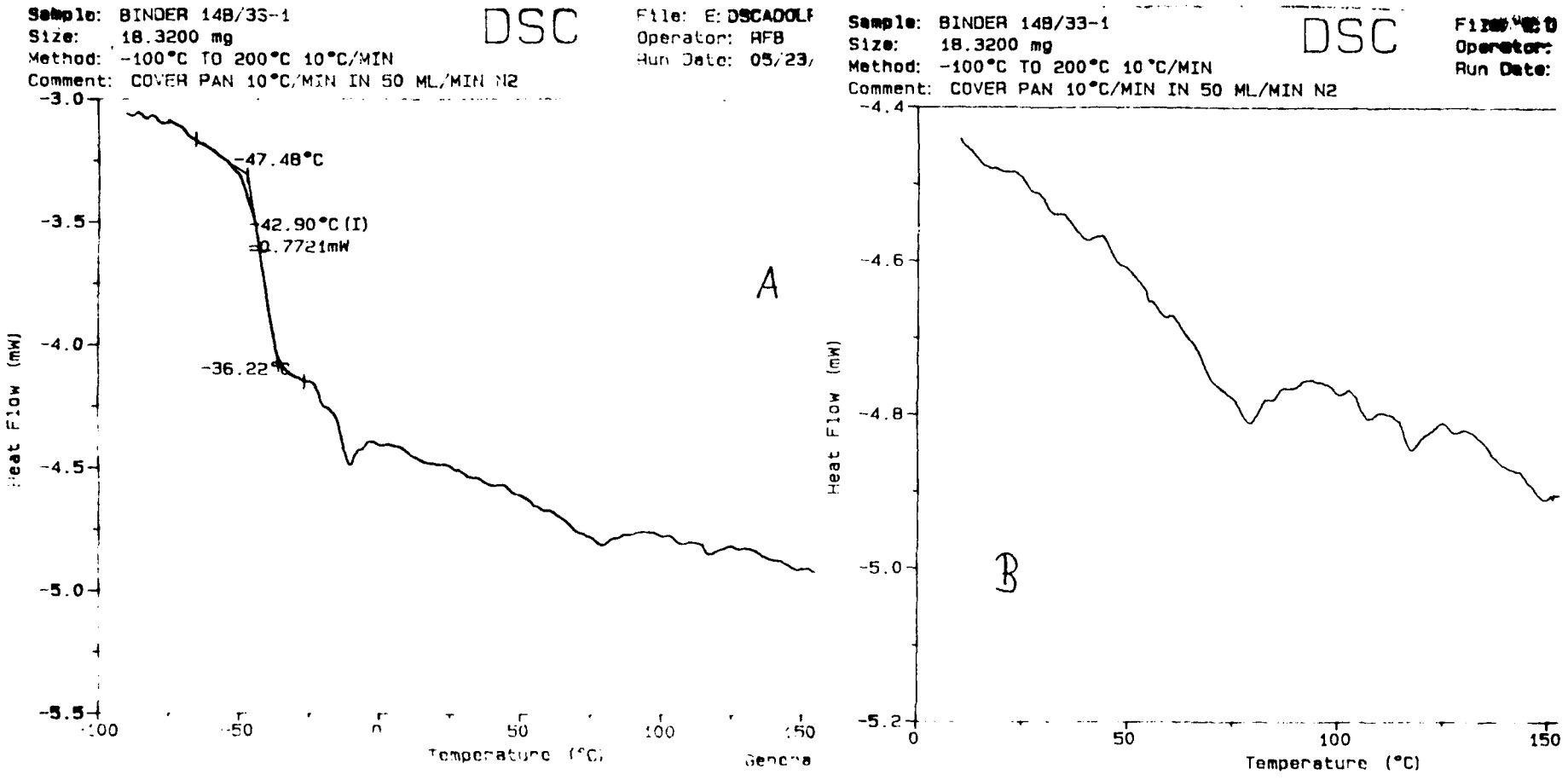


Fig. 36. DSC Curve of FPF-1 (5400)/TDI/Diol 7 Block Copolymer;
(A): Full Scale; (B): Expanded Scale

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1. Please correct the following error in your copy of the subject report: on p. 16, Table 10, the first entry in column 1 should read 9 instead of 13.

Horst Adolph

HORST G. ADOLPH
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